Development of a Flotation Process for the Recovery of Silver from Zinc Plant Residues

Final Report

by

Noranda Inc.
Pointe Claire, Quebec

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

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noranda

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ABSTRACT

This report investigates the feasibility of recovering silver in electrolytic zinc plants by flotation of leach plant residues.

Recent work and the literature on silver flotation are reviewed with attention being given to fundamental studies on the flotation of argentite, cerargyrite and native silver, and current zinc plant practice in the flotation of lead and silver from high acid leach residue.

Flotation testwork carried out by Noranda Research Centre with naturally occurring silver minerals, chemically precipitated equivalents of the natural minerals, and actual residues from Canadian Electrolytic Zinc and Kidd Creek Mines is reported. It is shown that the floatability of argentite, cerargyrite and native silver with sulphide collectors under acidic conditions, such as would be suitable for treatment of leach residues, is good, but that silver-bearing jarosite cannot be floated with sulphide collectors under acidic conditions. The flotation response of silver contained in actual residues is shown to vary from poor to good, depending on the source of the residue and the conditions under which it was produced. Conclusions and recommendations for further work are given.

RÉSUMÉ

Ce rapport étudie la possibilité de récupérer l'argent dans les usines de zinc électrolytique par flottation des résidus de l'usine de lixiviation.

Les travaux récents effectués dans ce domaine de même que les publications pertinentes sont passés en revue en mettant l'accent sur les études fondamentalles portant sur la flottation de l'argentite, de la cerargyrite et de l'argent natif ainsi que sur la pratique actuelle des usines de zinc en ce qui a trait à la flottation du plomb et de l'argent à partir des résidus de lixiviation très acides.

Le rapport fait également état de travaux effectués au Centre de recherche Noranda sur les minéraux naturels de l'argent, sur leurs équivalents chimiques obtenus par précipitation de même que sur les résidus provenant de Zinc électrolytique du Canada Limitée et de la Kidd Creek Mines. Il est démontré que la flottabilité de l'argentite, de la cerargyrite ainsi que de l'argent natif pratiquée sous conditions acides à l'aide de collecteurs de sulfures - par exemple dans le cas du traitement des résidus de lixiviation - est bonne, mais que cette technique ne peut être utilisée pour la flottation de la jarosite qui contient également de l'argent. Le rendement de la flottation de l'argent présent dans les résidus industriels variet de mauvais à bon selon l'origine des résidus et des conditions de leur production.

Conclusions et recommendations concernant les travaux futurs sont également présentées.

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Mineralogical examination of the zinc plant residues and the silver concentrates produced in this program was performed by J.E. Dutrizac and T.T. Chen of CANMET. Special thanks are also due to J.E. Dutrizac for preparation of the jarosite samples employed in the flotation studies.

SUMMARY

1. Silver recoveries in Canadian zinc plants range from 0% at Canadian Electrolytic Zinc (jarosite conversion process) to 50-60% at Kidd Creek (two-stage jarosite process) to >90% at Cominco and Hudson Bay, where the neutral leach residues are fed to either a lead blast furnace (Cominco) or a copper reverberatory furnace (Hudson Bay). Cominco, however, has embarked on a modernization program at Trail that may result in replacement of its lead blast furnaces with a unit that might not be able to accept all of its neutral leach residues, thus necessitating a separate residue treatment plant. There is thus considerable scope for improvement in the recovery of silver in the Canadian zinc industry.

This report presents the results of a literature review and experimental program conducted to evaluate the feasibility of recovering silver from zinc plant residues by flotation.

2. There is extensive literature on the flotation of silver-bearing ores, but relatively little on the fundamental floatability of silver minerals (argentite, cerargyrite, native silver, silver jarosite) believed to occur in zinc plant residues. The U.S. Bureau of Mines has investigated the flotation of argentite, cerargyrite and native silver as a function of pulp pH, particle size, collector and sulphidization, and reported good floatability with sulphide collectors in the pH range 7 to 11. Zinc plant residues are acidic, however, and furthermore, certain of the compounds contained in these residues may decompose under alkaline conditions with resultant excessive reagent consumption for pH control.

3. Fourteen published processes for flotation of zinc plant residue for the recovery of silver and/or lead and/or unroasted sphalerite employ widely varying conditions, suggesting that the flotation characteristics of residues from different plants (or

different residues from within a plant) vary widely and/or there is some lack of basic information on the flotation characteristics of the silver minerals in zinc plant residue. At the present time, only Vieille Montagne (high acid leach residue), Dowa (SO_2 reduction leach residue), Mitsubishi (sulphation roast leach residue) and Zhuzhou (neutral leach residue) employ residue flotation for the recovery of silver and/or lead.

4. Rougher flotation tests conducted under the present program with binary mixtures of sized (-200 +400 and -400 mesh) natural silver minerals (argentite, cerargyrite, native silver, tetrahedrite), synthetic silver minerals (chemically precipitated silver chloride, silver sulphide, silver jarosite and silver-bearing lead jarosite) and silver-doped pyrite and sphalerite with sand, have shown that, with the exception of the jarosites, all the silver minerals and compounds can be floated with high recovery (>90%) in acidic media (pH 3-7) with conventional sulphide collectors.

Silver jarosite and silver-bearing lead jarosites did not float with sulphide collectors under acidic conditions. Flotation with anionic oxhydryl collectors, such as oleic acid, under neutral or mildly alkaline conditions, however, resulted in 90-99% silver recovery.

5. Flotation tests under acidic conditions with zinc plant residues from Canadian Electrolytic Zinc (CEZ) and Kidd Creek resulted in silver recoveries ranging from 8 to 80%, depending on the type of residue and its source. These results, together with the demonstrated ready floatability of silver compounds believed to occur in zinc plant residue, indicate that the successful flotation of silver from residue requires that the leach conditions be controlled to maintain silver in a liberated and floatable form. The formation of silver-bearing jarosites must be avoided.

6. Locked cycle flotation tests (roughing and two stages of cleaning) with a CEZ pilot plant sample of neutral leach residue (0.03% Ag, 8.3% Pb, 22.1% Zn, 36.8% Fe, 2.2% S), in which the rougher pulp was sulphidized with 100 g/T $Na_2S \cdot 9H_2O$ prior to flotation and subsequent cleaning with dithiophosphate (R-3501) at pH 4.0, resulted in 77% silver recovery to a concentrate assaying 1.5% Ag, 1.5% Pb, 36.4% Zn and 12.0% Fe. The flotation concentrate (1.5 wt % of residue feed) also contained most of the unroasted sphalerite in the residue feed.

7. Roughing and cleaning flotation studies with a sample of CEZ pond residue (0.023% Ag, 0.5% Pb, 20.1% Zn, 36.6% Fe, 2.1% S), produced before the adoption of jarosite technology, and a variety of collectors at pH 3-5, resulted in silver recoveries of 42-46% to twice cleaned concentrates assaying 0.31-0.39% Ag, 0.06-0.08% Pb, 59-63% Zn and 6-9% Fe. The best results (0.39% Ag grade, 46% Ag recovery) with this oxidized and aged material were obtained by flotation with mercapto-benzothiazol (R-404) at pH 3.0.

8. Attempts to float silver from a sample of Kidd Creek high acid leach residue (0.149% Ag, 6.8% Pb, 4.1% Zn, 19.4% Fe, 10.4% S) and a pilot plant-produced sample of hematite residue (0.019% Ag, 0.8% Pb, 4.7% Zn, 43.8% Fe) were not successful, giving low silver recoveries and/or poor selectivity in flotation (low concentration ratios).

9. Mineralogical examination of the flotation concentrates produced from the CEZ pilot plant neutral leach residue and the CEZ pond residue showed that the silver occurred as rims of Ag_2S, $(Cu,Ag)_2S$ and Pb-Ag sulphide on sphalerite.

10. It is concluded that silver recovery from zinc plant residue by flotation is a viable process option, but successful application of this approach requires a good knowledge of the effect of leach chemistry on the form and occurrence of silver in residue. Work is therefore required to determine (i) the effect of leach conditions and calcine composition on silver flotation from residue, (ii) the degree of residue washing required to remove entrained leach liquor, and (iii) the effect of any flocculants used in residue thickening on the flotation process. The economics of residue flotation must also be assessed, including the impact of any required leach circuit modifications, additional liquid-solid separation equipment, changes to the plant water balance and loss of zinc to the flotation concentrate.

1. INTRODUCTION

Canada is the world's largest supplier of zinc concentrate and one of the major producers of zinc metal. Typical Canadian zinc concentrates contain 1-3 opt Ag, so that the silver input to a roast-leach-electrowin plant treating 250,000-400,000 tpy of concentrate (∿100-220,000 tpy Zn) amounts to 250,000-1,200,000 oz per year, with a current value of $2-10 M.

Silver recoveries in Canadian zinc plants range from 0% at Canadian Electrolytic Zinc (jarosite conversion process) to 50-60% at Kidd Creek (two-stage jarosite process) to >90% at Cominco and Hudson Bay, where the neutral leach residues are fed to either a lead blast furnace (Cominco) or a copper reverberatory furnace (Hudson Bay). Cominco, however, has embarked on a modernization program at Trail that may result in replacement of its lead blast furnace with a unit that might not be able to accept all of its neutral leach residue. This would necessitate a separate residue treatment plant.

One of the Canadian zinc plants (CEZ) has an accumulation of 800,000 tons of residue, produced prior to the introduction of jarosite technology, in storage ponds. These residues contain ∿6 opt Ag, with a current value of $40-50 M.

Roast-leach-electrowin zinc plants can concentrate silver in an "enriched" residue fraction by subjecting the neutral leach residue to a "high acid leach". This procedure, which is employed by a number of zinc producers in Europe, results in solubilization of large amounts of iron and would necessitate major changes to the flowsheets of Canadian zinc producers and the addition of considerable capital equipment. Furthermore, this "high acid leach" approach to residue enrichment (i) is not readily amenable to the treatment of either existing jarosite residues nor residues (jarosite, hematite) from new pressure leaching technology,

such as the Sherritt and hematite processes, and (ii) often requires subsequent concentration of the "enriched" residue by flotation to produce a saleable product.

It is apparent from the above that there is considerable scope for improvement in the recovery of silver in the zinc industry, and this improvement will be required for Canadian zinc plants to maintain their competitive position as producers of zinc metal.

On 25 August 1983, a contract was awarded to Noranda Mines Limited to undertake a study on the recovery of silver from zinc plant residues by flotation. The objectives were:

(i) To characterize the flotation behaviour of silver-bearing minerals commonly found in zinc plant residues.

(ii) To apply the flotation requirements determined for the flotation of silver-bearing minerals to the flotation of silver from zinc plant residues.

(iii) To determine the potential for recovering silver from zinc plant residues by flotation.

2. REVIEW OF LITERATURE

A review of the literature (1925-1983) on (i) the flotation of silver minerals and compounds believed to occur in zinc plant residues and (ii) flotation process proposed and/or applied to the treatment of zinc leach residues was conducted to determine the current state-of-the-art. The results of this survey are presented below. Bibliographies on publications dealing with (i) processes other than flotation for recovering silver and lead from residues and (ii) the treatment of polymetallic silver-bearing ores are given in Appendix I and Appendix II, respectively.

2.1 Flotation of Silver Minerals and Ores

2.1.1 Applied Research

Investigations into the concentration by flotation of silver values occurring in sulphide and oxidized ores have been carried out since the advent of flotation technology. The first results of reagent screening experiments in silver flotation were reported in 1931 by Gieser([1]). In order to increase the silver recovery from an oxidized ore, the effectiveness of a number of activators (metal salts)and collectors (organic-nitrogen sulphur compounds) was examined. Head and Thackwell([2]) performed a series of flotation tests with silver-bearing lead jarosite ore in which the floatability of various size fractions of the jarosite minerals was investigated with several collectors (sulphurated pine oil, oleic acid and xanthate). It was found that plumbojarosite floated best under neutral or slightly acidic conditions with fatty acid collectors. However, the fatty acids were not selective in separating jarosite from other minerals, especially calcite. Lauryl and octyl xanthates were found to be good collectors for plumbojarosite, giving 100% recovery at 3 lb/T addition, but the presence of ultrafine slimes of jarosite and other material in the naturally occurring ores presented problems. Sulphidization of the dry solids with hydrogen sulphide gas was attempted, but although the mineral surfaces seemed to be sulphidized, jarosite was depressed during flotation except when oleic acid was used as collector.

Zimmerly([3]) investigated the flotation of oxidized Ag-Pb ore using a modified grinding process prior to flotation. Prolonged grinding of naturally occurring silicious ores containing anglesite, cerussite, plumbojarosite,argentojarosite or cerargyrite in a steel mill produced highly metallized lead sponge and ferrous ion in solution. The lead and silver were subsequently recovered by flotation using xanthate as collector. The presence of NaCl in solution and elevated temperature during grinding (80°C) promoted the metallization of lead and resulted in an increased flotation recovery for silver and lead. This metallization grinding-flotation process produced concentrates with recoveries of

70-80% lead and 80-90% silver using amyl dixanthogen as collector. In order to elucidate the formation of sponge lead during grinding, single minerals were then examined with pure quartz. Anglesite and cerargyrite gave the highest lead and silver recoveries, and the highest lead metallization was obtained with anglesite. Cerussite and plumbojarosite showed metallization, but the flotation recovery was poorer than that of anglesite. Argentojarosite did not respond to metallization grinding-flotation. No follow-up has been reported.

Head([4]) investigated the mineralogical characteristics of oxidized silver-lead ores and factors affecting the concentration process. He found that, for the Tintic district ores in Utah, most of the silver occurred as metallic silver and was distributed in the dark varieties of anglesite and cerussite at sizes of several microns. Jarosites of lead and silver were also present. The problems in the flotation process were poor liberation of metallic silver from the lead minerals and the different floatabilities of anglesite, cerussite, and clean and dirty metallic silver.

A classic series of flotation tests using various silver minerals (cerargyrite, argentite, polybasite, tetrahedrite, proustite, etc.) mixed with ground sand was carried out by Leaver and Woolf([5]). They found that all the silver minerals, in the binary system with quartz, floated well with xanthate under neutral or mildly alkaline conditions and that, sulphidization (Na_2S) lowered the flotation of all silver minerals tested. Flotation under acidic conditions was not investigated. A test with cerargyrite using amyl xanthate at pH 7.9 resulted in a concentrate assaying 296 opt Ag with recovery of 98.2% from a head of 22.6 opt Ag. The tail assayed 0.45 opt Ag. A comparative test with sulphidization prior to flotation at pH 8.2 using 1 lb/T Na_2S gave a concentrate assaying 125.5 opt Ag and a tail assaying 16.85 opt Ag from a feed of 20.9 opt Ag. The silver recovery in the

concentrate was only 22.4%. An example with argentite showed that at about pH 7.0 xanthate flotation gave silver recoveries of over 98% from heads of 21 opt Ag. The tails assayed 0.25-0.31 opt Ag. On the other hand, after sulphidization at pH 7.5-7.8 with 0.25 and 0.5 lb/t Na_2S, the silver recoveries were reduced to 15.0 and 3.5%, respectively.

Futher tests with naturally occurring silver ores containing only one silver mineral gave a good silver recovery with xanthate. A sample containing only cerargyrite gave silver recoveries of 90-93%, even though the sample contained iron oxide slimes. Another sample containing only argentite gave similar results. On the other hand, samples of oxidized silver-lead ores containing other sulphide minerals gave only 70% silver recovery to a bulk flotation concentrate, and sulphidization of this sample did not affect the metallurgy. The low silver recovery was attributed to the tarnished nature of the metallic silver.

In continuation of the above work, Leaver and Towne([6]) carried out similar flotation experiments with sulfosalt-type minerals such as tennantite ($Cu_{12}As_4S_{13}$) and energite (Cu_3AsS_4), which normally contain silver. Selective flotation of these minerals from pyrite matrix was examined, and it was found that lime and cyanide were good depressants for pyrite if added in the correct amount. Sodium sulphide was of no use.

Engle and Jackson of U.S. Bureau of Mines conducted a series of flotation and cyanidation tests with a highly oxidized silver containing (16.7 opt Ag) ore([7]). The ore contained iron oxides (hematite, limonite, magnetite and ferric arsenate) and silicate gangue as major components. The only silver mineral detected was cerargyrite, which was found to be closely associated with hematite and limonite. Test results showed that 90-95% silver recovery was obtained to a concentrate assaying 3000 opt Ag with amylxanthate at pH 8.3 without sulphidization. The importance of the work is that silver chloride was shown to be readily floated with a simple sulphide flotation reagent.

There has been much work done on the flotation of silver by Russian workers([8-15]). However, most of their work was concerned with silver metal or its alloys, except the work of Skrobova and Zelenev([13]), Solozhenkin([14]) and Zelenev([15]). Skrobova and Zelenev examined the floatability of metallic silver and argentite with a number of collector reagents (ethyl, isoamyl and butyl xanthates, butyl dithiophosphate, etc.), and recommended specific reagent combinations. Solozhenkin([14]) investigated the adsorption of potassium-tetramethylpiperidine-1-oxyl-4-xanthate on silver mineral surfaces. It was found that the presence of pyrite promotes the adsorption of collector on the silver minerals (argentite, proustite, pyrargyrite and cerargyrite) through its high oxidizing activity toward xanthate. However, the adsorption of xanthate on cerargyrite was postulated as physical in nature.

The U.S. Bureau of Mines has published several reports on flotation studies with oxide([16,17]) and sulphide([18])ores containing gold and silver from various localities. In addition, Leaver([19,20]) has reported on the application of flotation,amalgamation, gravity concentration, cyanidation, roasting, or a combination of these processes to treatment of a number of gold-silver ores in the U.S. Conclusions concerning the best method of treatment were specific for each ore.

2.1.2 Fundamental Research

A comprehensive study on the electrochemical properties of silver sulphide-solution interface as a function of pH and ionic strength has been carried out by Freyberger and de Bruyn([21]). Silver and sulphide ions were identified as the potential determining ions in the pH range from 5 to 9, and within this pH region, H^+ and OH^- ions showed no specific affinity for the silver sulphide surfaces. The zero-point-of-charge for silver sulphide at fixed ionic strength with sodium acetate and sodium metaborate, which are indifferent ions, occurred at pAg 10. Above this pAg, an excess negative charge, and below this pAg, an excess positive charge were found at the solid interface.

Iwasaki and de Bruyn([22]) investigated the silver sulphide solution interface phenomena in the presence of sodium acetate and sodium nitrate at pH 4.7. Similar to previous work, they found the zero-point-of-charge of Ag_2S to be pAg 10.2 (6.8×10^{-9} g/L) and independent of the nature and concentration of the supporting electrolytes. It was also found that when the surface is positively charged, the adsorption density of silver ions was greater in acetate than nitrate solution. To elucidate the flotation of silver sulphide, the same authors reported additional work on silver-sulphide-amine system at pH 4.7([23,24]). They found that amine adsorption on the silver sulphide surface was dependent on pAg in solution, which is responsible for changing the surface potential of silver sulphide. The flotation behaviour of silver sulphide was correlated with the adsorption of dodecylammonium ion on the surface, and it was found that the adsorption of amine on silver sulphide surfaces at pH 4.7 was strongly dependent on the pAg. A shift in the zero-point-of-charge towards a lower pAg due to the adsorption of amine indicated a specific affinity of dodecylammonium ion towards silver sulphide surfaces, and the adsorption of undissociated amine molecules at pH 9.2 was independent of the interfacial electrical conditions.

Flotation theory, in general, has been developed through the measurement and interpretation of electrokinetic phenomena in the specific mineral-water system. For oxide minerals, H^+ and OH^- ions are the potential determining ions which affect the interfacial electrical conditions, and thus control the interactions between the charged solid surface and ionized chemicals in the system. On the other hand, with sparingly soluble salts and most of the sulphide minerals, the potential determining ions are the lattice ions as well as H^+ and OH^-.

Electrokinetic and solubility data for various species possibly occurring in the zinc leach residues are compiled in Table I.

TABLE I

THE POINT-OF-ZERO-CHARGE AND SOLUBILITY DATA FOR SOME MATERIALS FOUND IN ZINC LEACH RESIDUES

Species	Point-of-zero-Charge	Remarks	Solubility Product	Reference
AgCl	pAg 4.0 (1.08×10^{-2} g/L)	$AgNO_3$ and KCl	1.56×10^{-10}	25 26
Ag_2S	pAg 10.2 (6.8×10^{-9} g/L)	H_2S added to ammoniacal AgOH Na_2S and excess $AgNO_3$ at pH 4.7	6.3×10^{-52}	21 26
$PbSO_4$	pPb 2.1 (1.65 g/L)	Precipitated $PbSO_4$	1.06×10^{-8}	26 27
$CaSO_4 \cdot 2H_2O$	positive pH 2.3-10.7	$CaCl_2$ added to Na_2SO_4 Natural $CaSO_4 \cdot 2H_2O$	2.4×10^{-5}	26 33
Goethite (FeOOH)	pH 6.8	Natural Goethite	-	28
Hematite	pH 6.7 pH 3.0-6.7 pH 8.6	Natural, (Minn.) Natural, (Itabira) Synthetic	- - -	28 29 30
SiO_2	pH 1-2 pH 2-3	Silica gel α-quartz	- -	31 31
Sulphur	pH 2.0	α-sulphur	-	32
ZnS	variable	-	2.6×10^{-24}	65

2.2 Silver Ion Flotation

Recovery of dissolved metals from aqueous solutions by ion or precipitate flotation techniques has been known for a long time. Precipitate flotation has been practiced mainly in the treatment of oxide copper ores (Leach-Precipitation-Flotation Process), and various water treatment systems in hydrometallurgical and mining operations, in which the contained metals are precipitated as less soluble compounds such as sulphides, oxides, hydroxides and organo-metallics.

The flotation of dissolved silver ions from aqueous solutions is not directly related to zinc hydrometallurgy, however, the flotation characteristics and reagent systems may be useful in identifying conditions for silver recovery from zinc leach residues.

Nash([34]) has described a process for the recovery of ultrafine silver halides from photographic waste solution. Photographic waste water containing 30-100 ppm silver halides was treated with activated sodium silicate and sodium hydroxide to encapsulate the silver values. Dissolved air flotation is used without a specific collector. The sodium silicate carries the silver halides and floats to the surface with the air bubbles generated by the sudden release of pressure. It is claimed that the tail stream contains only 0.5 ppm silver halide.

Another recent patent([35]) describes a similar process of recovering silver and silver halides from a photographic waste water. The process involves treatment of the waste water with protein at the iso-electric point of the protein, usually at about pH 4. Flotation of the silver and silver halide-laden protein is then carried out by blowing finely dispersed inert gas bubbles. The recovery process is further accelerated by the addition of a tencide, a cationic polyelectrolyte.

Work on silver recovery from silver thiosulphate-containing photographic waste solution has also been reported in recent years. Charewicz and Niemiec([36]) carried out a series of flotation tests using a cationic collector (hexadecyl diethyl ammonium chloride) at various solution pH and silver complex concentrations. They found the optimum silver flotation was at pH 5.0. The results were correlated with the activity of collector, pH and equilibrium in the aqueous system containing Ag^+, $S_2O_3^=$ and H_2O. Bhattacharyya and Grieves([37]) have investigated the flotation regions of $Ag(S_2O_3)^-$, $Ag(S_2O_3)_2^{-3}$ and Ag_2S using cationic surfactants at various solution pH values. The results were discussed in terms of the stoichiometric ratios of thiosulphate to silver, silver to surfactant, surface potential and precipitate size. Butyl and isopropyl xanthate collectors have been used for the recovery of silver from photographic solution by Amaryan and others([38]). The most complete flotation of silver occurred at pH 4 and at 1:1 ratio of xanthate and contained silver. Complete silver recovery was obtained from a solution containing 0.25 g/L Ag.

2.3 Flotation of Silver and Lead From Zinc Plant Residues

The first experimental work dealing with the flotation of zinc leach residue was reported by Chibulka in 1962([39]). He initially carried out a series of basic experiments to define the flotation characteristics of PbS, $PbSO_4$ and Fe_2O_3 in terms of collector adsorption and sulphidization. Sulphidization followed by flotation using ethyl xanthate was found effective in separating lead sulphate from iron oxide and silica. It was speculated that it should be possible to produce a lead concentrate having 40% grade with 90% recovery. No details were given on the flotation conditions.

Riskin and others([40]) investigated the use of Waelz furnace clinker as copper precipitant in the leach-precipitation-flotation (L-P-F) process for oxide copper. The copper and precious metals contained in the clinker were recovered by flotation along with the cement copper. It

was reported that metal recoveries of 87.7% copper, 84.3% gold and 87.6% silver were obtained. Rosinger and others have described a flotation process for the recovery of metals from zinc Waelz furnace clinkers([41]). The clinker (0.7-3.0% Cu, 3.7% Zn and 50-150 g/t Ag) was ground to minus 200 mesh and conditioned with water glass (600 g/t, ethyl xanthate (50 g/t) at pH 6-7 and 20% solids. The conditioned pulp was then floated with non-ionic frother (400 g/t) for about 1 h. The cleaner concentrate assayed 12-13% Cu, 13-15% Zn and 900-1000 g/t Ag with recoveries of 80% copper and silver.

The original zinc leach and residue treatment plant at the Akita Zinc Plant of Mitsubishi Metal Mining Company has been described by Moriyama and Yamamoto([42]). At the residue treatment plant, the washed residue (basically a ferrite residue) was repulped and conditioned with Aero 404 promoter (Mercaptobenzothiazole) between pH 1-5, and floated with MIBC as frother to recover unoxidized Ag_2S. It is claimed that 75-80% silver recovery was obtained. The schematic flowsheet is shown in Figure 1. This flotation process at the Akita Zinc Plant was basically meant to float unroasted zinc sulphide, along with the silver, from the ferrite residue.

Modification and improvements to the silver recovery operation at the same plant have been described by Yamamoto([43]) at the AIME meeting in 1977. Mineralogical examination of the residue revealed that the silver occurred as both metallic silver and argentite, and that the argentite particles were mostly present as lockings with sphalerite. The highly oxidized nature of the residue caused the flotation rate to be extremely slow compared to normal sulphide flotation, and it was found that the low floatability could be overcome by close pH control and the use of dispersant. The flotation conditions were similar to the original process described above.

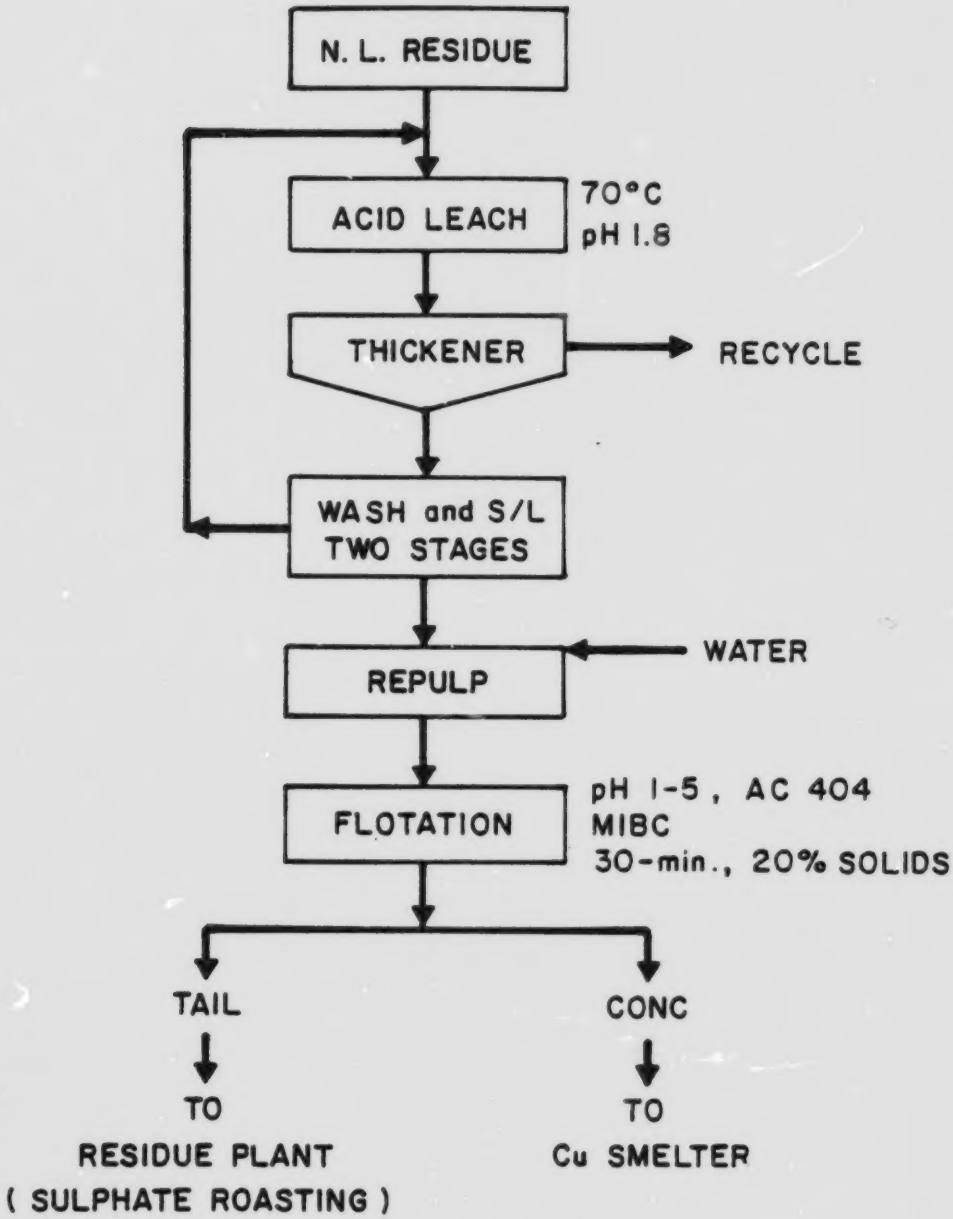

Figure 1 - Original Flowsheet of Mitsubishi's Akita Zinc Plant

Further developments in the treatment of ferrite residue at the same plant has been reported recently([44]). The ferrite residue is roasted with pyrite as sulphatizing agent at a temperature of 650-700°C (Figure 2). The calcine is then leached in three stages, including the air oxidation of iron with calcium carbonate addition for pH control. After solids/liquid separation, the residue is sent to flotation, while the liquid is recycled to the acid leach circuit. In the flotation stage, more than 80% of the silver in the residue is recovered using AC 404 at pH 3.5-4.0. An extended flotation time is required to obtain a satisfactory recovery. Microscopic examination of Mitsubishi's flotation feed has shown that the silver is present as argentite associated with sphalerite. Some metallic silver as well as metallic gold and electrum (gold-silver alloy) have also been observed. The recovery of fine silver (minus 5 microns) and silver in the coarse gypsum particles (plus 200 mesh) is not as good as that of silver between minus 200 mesh plus 5 microns, and constitutes the main source of silver loss. Some of the silver seems to become enclosed by the gypsum precipitate during the leaching and air oxidation stages. About 7000 TPM of sulphate leach residue is treated in flotation, with about 80% silver recovery being obtained from a head assaying 1.7 g/t Au and 215 g/t Ag. Although the residue contains 4.2% Pb, no lead recovery by flotation has been reported. Although the details of the residue are not known, old stockpiled residues (70-100 g/t Ag) are also being treated for silver recovery under similar flotation conditions at a rate of 5000 t/M. About 50% silver recovery is being realized.

At Espanola del Zinc, the ferrite residue is treated by flotation to recover unroasted zinc sulphide([45]) using a process similar to the old practice at Akita. The flotation is carried out in electrolyte medium containing 30-35 gpL Zn using ethyl xanthate at pulp pH 5.0-5.5. In order to obtain good flotation, copper sulphate activation of sphalerite is required. The flotation concentrate is recycled to the roaster and the tailings are sent to a subsequent pyrometallurgical treatment. Lead and

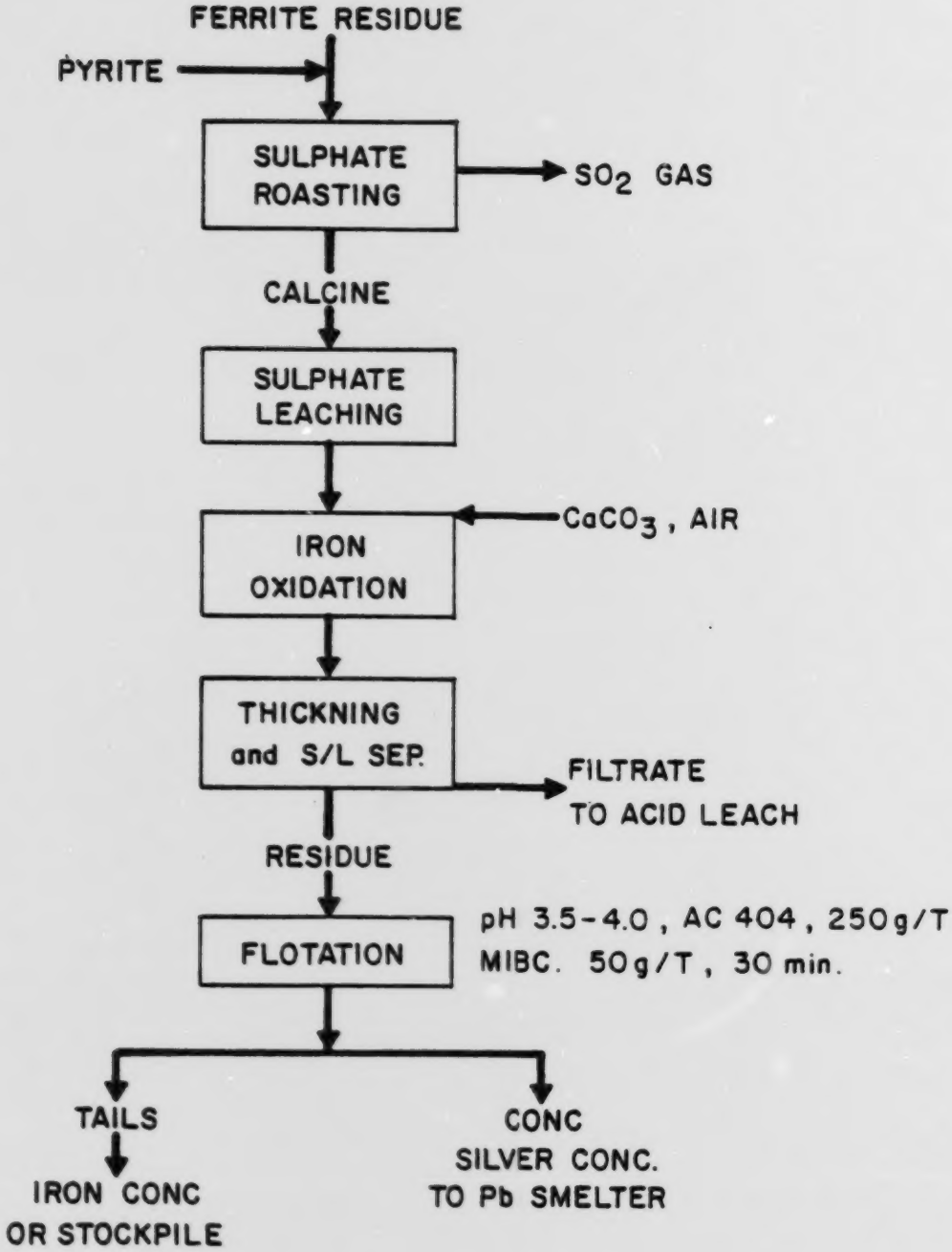

Figure 2 - Flowsheet of Present Silver Recovery Process at the Mitsubishi Akita Zinc Plant

silver recovery is not included, because the calcine contains very low lead and silver (1.5% Pb and 55 ppm Ag). 65-75% of the sulphide zinc in the feed is recovered to the concentrate. This corresponds to 11-13% zinc recovery from the residue.

The operation of Akita Zinc Company has been described by Mealey([46]) and Koh([47]). The company is a consortium formed by six Japanese mining companies and operated by Dowa Mining Company. The plant has a monthly capacity of 6,500 MT of slab zinc. After roasting the zinc concentrate and neutral leaching of calcine, the ferrite residue is leached in a reducing atmosphere with SO_2 to solubilize the zinc and iron in the ferrite. The leach slurry is treated with hydrogen sulphide prior to flotation to precipitate copper. The resulting solids containing copper precipitate, precious metals, lead and gangue are filtered and sent to the Dowa copper smelter for separate treatment by flotation. In normal operation, a copper concentrate containing gold and silver, and a lead concentrate are produced.

The first Dowa process([48]) involved leaching of ferrite residue with sulphuric acid and SO_2, a decopperizing stage using H_2S as copper precipitant and flotation of the resulting residue (Figure 3). The washed residue was repulped and floated at pulp density of 10% solids and pH 2.0 for about 20 minutes using kerosene (4100 g/t) as collector and Dowfroth 250. The flotation tails were then classified to separate fine lead sulphate from the bulk of coarse silicate gangue. Composite results from the patent are given in Table II. According to the description in the patent, the H_2S precipitation served not only to precipitate copper but also to remove any harmful elements in the zinc electrolyte, such as bismuth and arsenic.

Improvements in the treatment of ferrite residue, including flotation, at Akita Zinc Company were reported by Ohtsuka([49]). Developments involved (i) the addition of elemental sulphur in the leach, (ii) recognition of the relationship between the H_2S dosage and the floatability

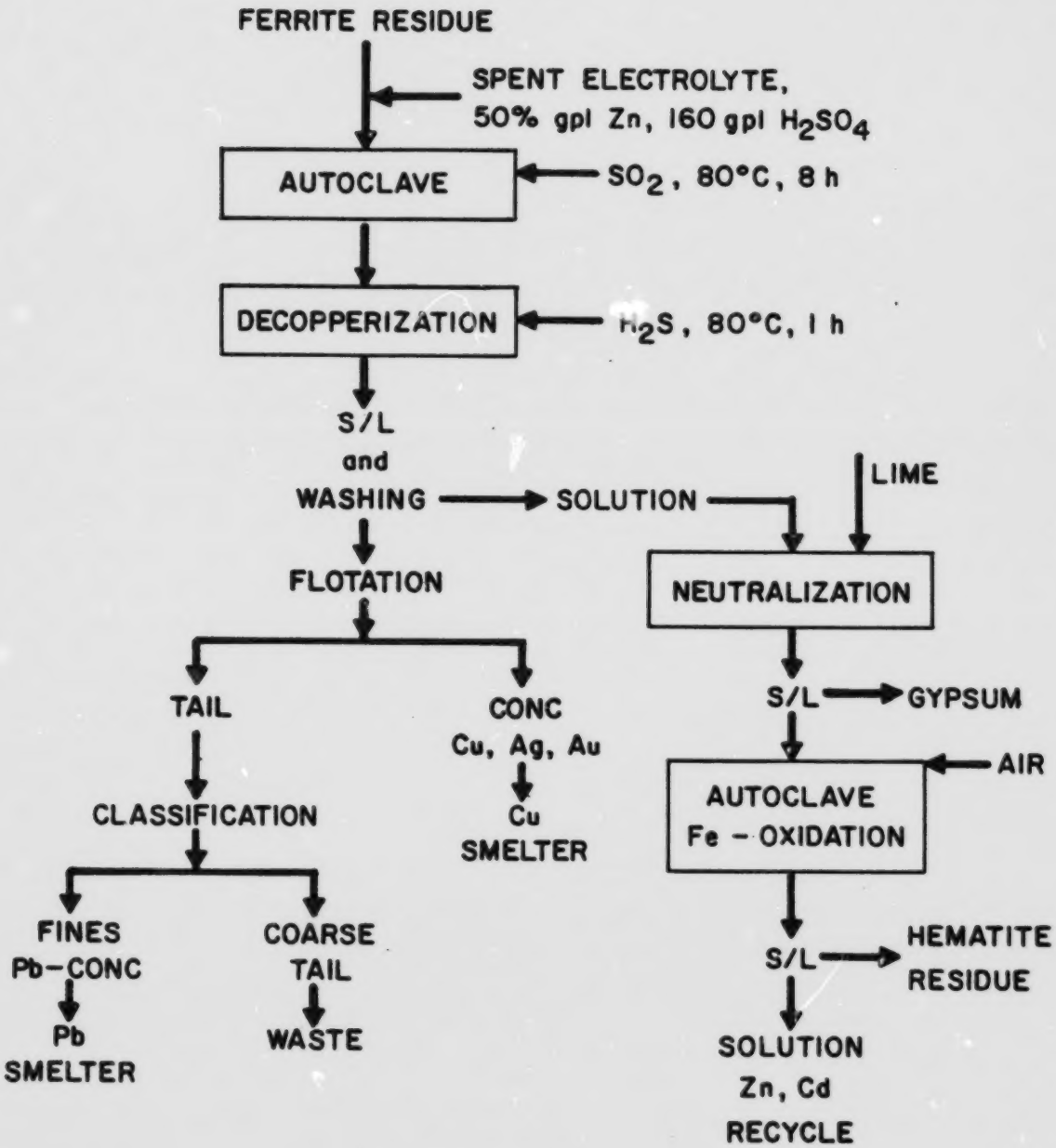

Figure 3 - Flowsheet of Original Dowa Residue Treatment Process
(Japanese Patent 48-7961)

TABLE II

CALCULATED GRADES AND RECOVERIES IN DOWA RESIDUE TREATMENT CIRCUIT

	Cu-PM Conc.		Pb-conc. Cyclone O/F		Tails,Cyclone U/F		Flotation Feed	
Element	Assay g/T, %	Recovery %	Assay g/T, %	Recovery %	Assay g/T, %	Recovery %	Assay g/T %	Recovery %
Au	61.3 g/T	95.0	1.6 g/T	3.3	0.6	1.9	16.1 g/T	100.0
Ag	6587	93.0	245	4.6	100.0	2.4	1770	100.0
Cu	24.9 %	95.0	1.0 %	3.0	0.3	2.0	6.5 %	100.0
Pb	4.0	4.2	42.5	59.8	20.5	36.0	23.7	100.0
Zn	3.3	29.5	2.5	29.7	2.7	40.8	2.8	100.0
Fe	4.0	26.3	4.0	35.1	3.5	38.6	3.8	100.0
S	21.0	41.3	10.0	26.3	9.88	32.4	12.7	100.0

of copper, and (iii) changes to the reagent schedule for copper and lead flotation. Elemental sulphur addition serves to enlarge the size of the copper sulphide precipitate. Copper ions seem to diffuse into sulphur, so that the size of the resulting copper sulphide precipitate is increased by the elemental sulphur, which has high flotation characteristics. The amount of H_2S blown into the precipitation stage has an effect on the flotation of copper, silver and lead, and in order to float separate concentrates of copper plus silver and lead, the quantity must be controlled to prevent the sulphidization of lead. This is accomplished by controlling the redox potential of the system.

Details of the flotation process were not disclosed, however, it was noted that KL#274, presumably a dithiophosphate-type collector, for copper precipitate and silver was found to be effective. The tails of the copper flotation are floated with n-alkyltriethyldiamine, a cationic collector to recover lead. The final tails after lead flotation are used as flux at the nearby copper smelter to reduce the silver losses. It is reported that recoveries of 97% silver, ∿100% copper and 83% lead are obtained in the flotation process.

Another Dowa process for the recovery of copper, gold and silver from the zinc leach residue has been described([50]), but is apparently not operated commercially. The process is similar to the process mentioned above, except that the ferrite residue is subjected to a sulphation roast in order to increase the solubilization of zinc, cadmium, copper and other elements (Figure 4). Flotation of copper and precious metals is performed with washed and ground residue using kerosene and Aeropromoter 404 as collectors and MIBC as frother. The pulp pH is 2.8-4.9, depending on the washing, and 20-45 min. of flotation time are required to obtain reasonable recoveries. It is claimed that recoveries of over 90% copper, and silver, and about 70% gold are obtained.

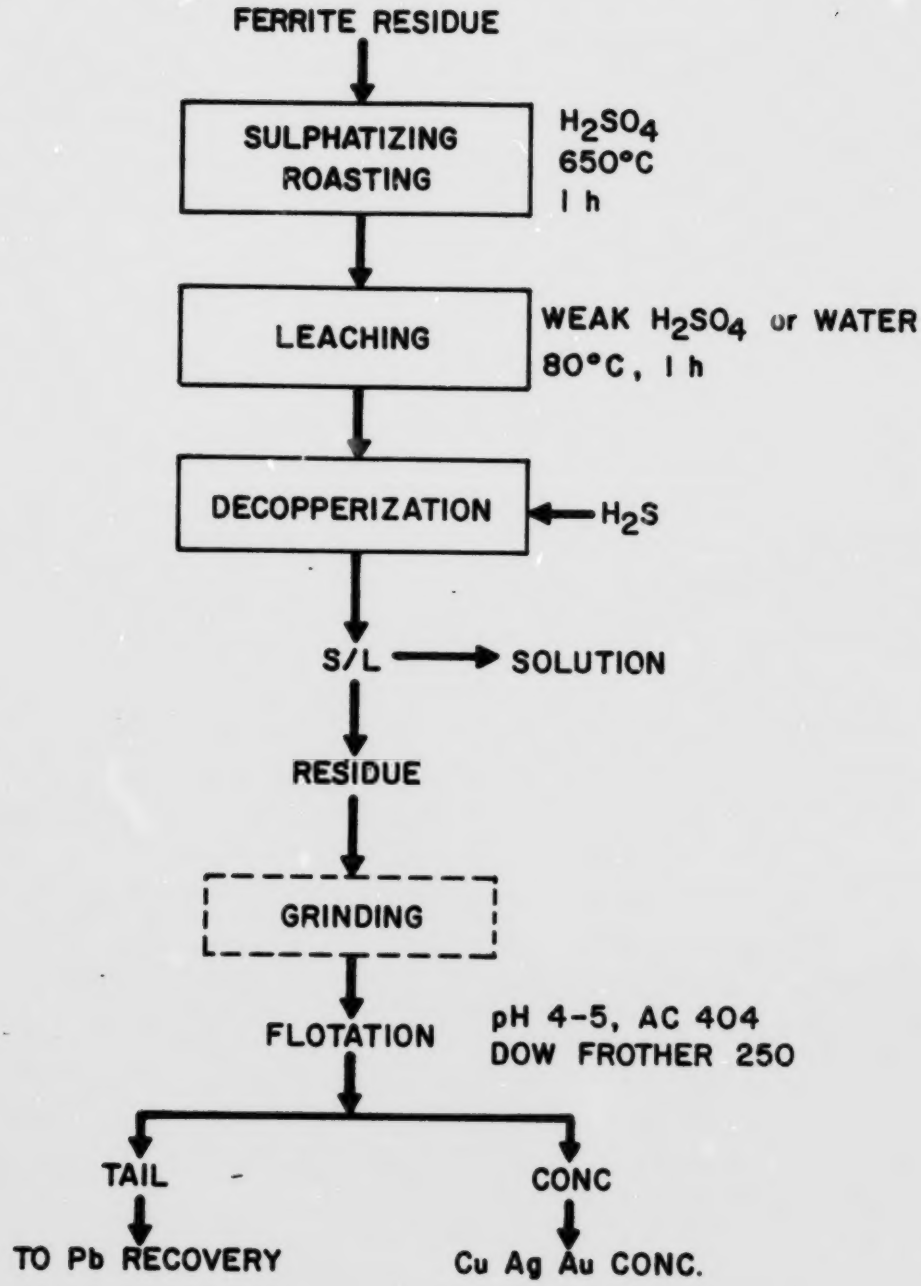

Figure 4 - Flowsheet of Modified Dowa Residue Treatment Process
(Japanese Patent 49-10881)

A flotation process for the recovery of silver and lead from high acid leach residue is described in a patent assigned to Asturiana de Zinc S.A.([31]). According to the process the residue can be treated in one or two stages for floating silver and lead together or separately, depending on the residue characteristics. The normal silver flotation is carried out at pH 2.0-4.5 using conventional sulphide collectors, dispersant (preferably sodium silicate) and frother. In this first stage, elemental sulphur and unreacted zinc sulphide are also floated with silver. The second stage flotation is carried out on the first-stage tails, after activation of the lead sulphate with sodium sulphide, using xanthate or dithiophosphate collectors. Single stage flotation for recovery of silver and lead simultaneously can be used, but silver losses to the tails increase due to the depressing action of H_2S on silver. The success of the process primarily depends on the basic matrix of the residue, such as the content of jarosite and neutralizing agent used after leaching. A typical two-stage flotation result obtained according to the patented process is reproduced in Table III.

TABLE III

TYPICAL FLOTATION RESULTS FOR ASTURIANA PROCESS

Fraction	wt %	Assay, %				Distribution, %			
		Pb	Zn	Fe	Ag g/T	Pb	Zn	Fe	Ag
Ag concentrate	5.0	5.5	30.2	2.3	14,300	1.00	38.70	4.66	59.45
Pb concentrate	46.0	55.5	3.6	3.2	900	91.46	42.45	59.31	34.42
Tailings	49.0	4.3	1.5	1.8	150	7.54	18.85	35.73	6.13
Feed	100.0	27.9	3.9	2.5	1,202	100.0	100.0	100.0	100.0

A South African Patent Application by Vieille Montagne([52]) describes a process for treatment of its very high acid leach residue at Balen. The residue, containing metallic silver, silver sulphide or silver sulfo-arsenide, silver chloride, lead sulphate, silica, iron oxide, calcium sulphate, unreacted zinc sulphide and elemental sulphur, is filtered and washed and then fed to the flotation circuit where two-stage flotation is carried out at natural pH (1-5) with conventional sulphide collectors and an anionic oxhydryl collector for silver and lead. The first stage silver concentrate contains any unreacted zinc sulphide and the elemental sulphur in addition to silver. The lead concentrate contains mainly lead sulphate. The formation of jarosite-type materials in the leach affects the recoveries of silver and lead. Therefore, careful leach circuit control to avoid jarosite formation is a main factor in residue treatment. It is also interesting to note that the process does not utilize sulphidization to float lead. A silver concentrate assaying about 10,000 g/ton Ag is produced at about 85% Ag recovery, and a lead concentrate assaying ∿50% Pb is produced at about 65% recovery. The lead flotation with anionic oxhydryl collector is reportedly enhanced by subjecting the pulp to temperature over 50°C. The process actually employed at Balen is believed to be similar to that described in the patent application.

A recent British Patent Application([53]) by Outokumpu Oy describes a flotation process for the recovery of silver and lead contained in several types of iron-bearing residues. In this process, the material is sulphidized in closed tanks at pH 3-6 and 50-80°C for 2-6 hours. Sodium sulphide is continuously added during this period in an amount sufficient to convert the contained lead and silver to sulphides. Also lead and silver sulphide seed are added to the pulp to provide nuclei so that the lead sulphide and silver sulphide will precipitate on the seed particles. The sulphidized slurry is then floated at pH 2-4 with conventional sulphide collectors. Recoveries of 93% silver, 86% gold and 91% lead are reported. This sulphidization-flotation process is

claimed to be applicable to ferrite residue, hematite residue and residue from sulphation-roast-leach processes, but it is not being employed commercially at this time.

A similar process for the treatment of jarosite residue has also been disclosed([54]) by Outokumpu Oy. In this process, jarosite residue is leached with H_2SO_4 at 95°C for 2 hours to produce a solution containing $Fe_2(SO_4)_3$ and Pb-Au-Ag containing solids. After the jarosite decomposition, the remaining solids are separated and washed. This leached residue is then sulphidized prior to flotation as described above. Over 90% lead, silver and gold recoveries are claimed.

Recently, a report on the flotation of silver from ferritic leach residue was published by the staff of the Zhuzhou smelter in China([55]). According to the report, silver in the residue occurs as silver sulphide (61.8%), metallic silver (10%), silver chloride (3.5%) and silver in gangue (17.1%), and flotation under acidic conditions (unspecified)with 400-500 g/t black distillate, presumably a kind of dithiophosphate, and MIBC gave the best results. Furthermore, it was reported that a small amount of sodium sulphide addition was beneficial in the silver flotation, because of its surface cleaning action. Silver concentrates assaying 6,000-20,000 g/t Ag are obtained with recovery of 60-75%, depending on the feed grade. It is also of interest that the type and amount of flocculant used in the leaching stage has an effect on the silver recovery.

A flotation process for the recovery of lead sulphate from zinc leach residue or steel mill dust has been described in a Japanese patent([56]). The low acid leach residue is floated prior to high acid leaching step using amine acetate, alkyl sulphonates and aryl dithiophosphate as a collector set at pH below 3.0, and the use of depressants, such as starch or gum arabic, for depression of iron oxide is highly recommended.

It is claimed that it is possible to produce a concentrate containing over 40% Pb with recovery of about 80% from a feed containing 5.5-11.3% Pb. It is mentioned that silver and zinc sulphide were also recovered, but no data were given.

A paper presented at the 1984 AIME meeting by Mendoza outlines the flotation operation at the Torreon zinc plant of MET-MEX Penoles([57]). The high acid leach residues are floated for silver with Teefroth A at pH 2 and the tails are then floated for lead using sulphonate as collector. No other details on flotation are provided. A mineralogical study of the residue showed that the lead occurs as lead sulphate and fine lead sulphide enclosed in jarosite, and the silver occurs as sulphide locked in jarosite as well as argentojarosite.

Cristovici and others have carried out a series of experiments to investigate the flotation of residue obtained from the sulphation-roast-leach process developed by the New Brunswick Productivity Council (RPC)([58]). The roasted material was leached with dilute sulphuric acid to extract the easily soluble constituents, and then leached with strong hot acid to solubilize the zinc ferrite and other materials. The lead and silver are not solubilized and remain in the leach residue. Flotation was carried out at pH 9-10 with conventional sulphide collectors, after a short period of sulphidization in stages. Concentrates containing 22% Pb and 600 ppm Ag were produced with recoveries of 85% lead and 77% silver from a feed assaying about 10% Pb and 290 ppm Ag.

High gradient magnetic separation has also been investigated([59]) for treatment of the sulphation roast-leach residue (20.5% Pb and 0.03% Ag). The best results obtained were a Pb-Ag concentrate assaying 31.5% Pb and 0.06% Ag, with recoveries of 81% lead and 77% silver. The low recovery was attributed to the physical characteristics of the residue (agglomerates of lead sulphate and hematite particles or coating of lead sulphate by ultra fine hematite)

Espinosa-Gomez and Finch also examined the feasibility of separating hematite from lead and silver in the high acid leach residue obtained from the sulphation roast-leach process using high gradient magnetic separation([60]). Concentrates assaying 34-47% Pb and 450-550 ppm Ag were produced with recoveries of 65-95% lead and 60-85% silver from a feed of 25% Pb and 380 ppm Ag.

A summary of the published flotation processes for treatment of various zinc plant residues is presented in Table IV. Fourteen processes are listed and it is believed that six of them are or have been in commercial operation.

2.4 Conclusions

1. There is extensive literature on the flotation of silver-containing ores, but relatively little on the fundamental floatability of silver minerals (argentite, cerargyrite, native silver, silver jarosite) present in the zinc plant residues. The U.S. Bureau of Mines has investigated the flotation of a number of silver minerals as a function of pulp pH, particle size, collector and sulphidization, but this work was performed in the pH range 7-11. Zinc plant residues are acidic, and certain of the compounds contained in these residues will decompose under alkaline conditions.

2. Approaches to the flotation of zinc plant residue for the recovery of silver and/or lead and/or unroasted sphalerite vary widely, suggesting that the flotation characteristics of residues from different plants (or different residues from within a plant) vary widely and/or there is some lack of basic information on the flotation characteristics of the silver minerals in zinc plant residue. At the present time, only

TABLE IV

SUMMARY OF FLOTATION PROCESSES APPLIED TO ZINC PLANT RESIDUES

	MITSUBISHI I	MITSUBISHI II	ESPANOLA del ZINC	DOWA I	DOWA II	DOWA III
Type of residue used Major component	low acid leach residue 21% Zn, 4.6% Pb 34.5% Fe, 352 g/t Ag, zinc ferrite	residue from sulphate roast-leach of ferrite residue 45% Fe, 215 g/t Ag, 4% Pb iron oxide, gypsum	acid leach residue 25% Zn, 29% Fe zinc ferrite	reduction leach residue, precipitated with H_2S 1700 g/t Ag, 24% Pb $PbSO_4$, silicates	same as Dowa I except elemental sulphur is added to the leach	sulphate roast-leach residue after H_2S precipitation silicates, $PbSO_4$, iron oxide
Filtration and washing	filtration with 2 stages of washing	filtration with 2 stages of washing	filtration and washing. Pulp contains 30-35 gpl Zn	Yes	Yes	Yes
S..hidization pH time quantity	No	No	No	H_2S precipitation of dissolved Cu, Bi, Sb	H_2S precipitation of dissolved Cu, As. Excess addition activates $PbSO_4$	H_2S precipitation of dissolved Cu, Ag
Flotation pH time collectors other reagents recovery	one-stage 1-5 30 min. Mercaptobenzothiazole (R 404) MIBC frother Ag: 75-80% Au: 30-40% no lead recovery	one-stage 3.5-4.0 Mercaptobenzothiazole (R 404) MIBC frother Ag: 75-80% Au: 20-30% no lead recovery	one-stage 5-5.5 Ethyl xanthate $CuSO_4$ No attempt for silver flotation	one-stage 2.0 30 min. Kerosene Dowfroth 250 Ag: 93% Au: 95% Cu: 95%	two stages 2.0 30 min. KL#274 for Cu and Ag diamine for Pb Dowfroth 250 Ag: 97% Cu: 100% Pb: 83%	one-stage 4-5 Mercaptobenzothiazole Dowfroth 250 Ag: 92% Cu: 93%
Limitation	pH control and dispersion are required	coarse gypsum enclosed silver		H_2S precipitation controls the recovery of Cu and Ag	H_2S precipitation requires good control	grinding may be required
Status and flotation concentrate	operated at 300 tph capacity unroasted ZnS is also recovered metallic Ag Ag_2S in ZnS	in operation metallic Ag and silver, zinc sulphide	in operation to recover unroasted ZnS for recycling to the zinc sulphide	patented No lead recovery by flotation, instead cycloning is used Cu sulphides and silver	in operation Ag with Cu sulphide and $PbSO_4$	patented Ag with Cu sulphide

TABLE IV (cont'd)

SUMMARY OF FLOTATION PROCESSES APPLIED TO ZINC PLANT RESIDUES

	ASTURIANA	VIEILLE MONTAGNE	OUTOKUMPU I	OUTOKUMPU II	ROMANIA	ZHUZHOU	TOHO	MET-MEX PEÑOLES
Type of residue	high acid leach residue	high acid leach residue	neutral leach residue or hematite residue	leached jarosite residue	Waelz clinker	neutral leach	neutral leach	high acid leach
major component	silicates, $PbSO_4$, jarosite	$PbSO_4$, silicates, S^o iron oxide, gypsum	zinc ferrite, ZnS, hematite, silicates, gypsum		0.7-3% Cu, 3-7% Zn, 50-150 g/t Ag iron oxide	300-400 g/t Ag, 20% Zn, 3-4% Pb, Zn ferrite	5% Pb, 20% Zn 33% Fe Zn ferrite	5% Zn, 7.5% Pb 800-900 g/t Ag, 10% Fe Jarosite
Filtration and washing	may require filtration and washing	Yes	Yes	Yes	No	unknown	unknown	unknown
Sulphidization pH time quantity	superficial sulphidization to activate $PbSO_4$	No	Pb and Ag are converted to sulphides 2-5 3-4 h	Pb and Ag are converted to sulphides 2-6 3-4 h	No	superficial sulphidization not known not known 130 g/t	No	No
Flotation pH time collectors	one or two stages 2-5 Sulphide collectors for silver and lead	two stages 1-4 sulphide collectors (Z-200, R 242) for Ag and alkyl sulphonate for lead	one stage 2-4 Sulphide collectors	one stage 2-4 sulphide collectors	one stage 6-7 1 h ethyl xanthate	with cleaning unknown dithiophosphate	simple 2-3 (2.7) primary amine dithio phosphate alkyl sulphonate	two stage 2 - none for Ag sulphonate for Pb
other reagents	sodium silicate		dispersant	dispersant	Na_2SiO_3	MIBC	arabia gum frother	frother
recovery	Ag: 94% Pb: 92%	Ag: 90% Pb: 90%	Ag: 94% Pb: 85% Au: 84%	Ag: 95% Pb: 94% Au: 88%	Au Ag 80% Cu	Ag:65-70%	Pb: 81-85%	Ag: 90% Pb: 80%
Limitation	the presence of jarosite affects the recovery as well as the grade	the presence of jarosite should be avoided. high pulp temperature flotation in Pb circuit	Pb and Ag sulphide seeds, long sulphidization in the closed tank, raised pulp temperature	Pb and Ag sulphide seeds, long sulphidization in the closed tank. raised pulp temperature	clinker is ground to minus 200 mesh	use and quantity of flocculant in leach affects the recovery	-	-
Status and flotation concentrate	patented Ag minerals, S^o and ZnS with $PbSO_4$	in operation Ag_2S with S^o and ZnS, $PbSO_4$	patent Pb-Ag conc.	patent Pb-Ag conc.	patent Cu-Ag-Au	operated 100 t/d unroasted sulphide is also recovered	patent no silver recovery is mentioned	plant operated

Vieille Montagne (high acid leach residue), Dowa (SO_2 reduction leach residue), Mitsubishi (sulphation roast leach residue) and Zhuzhou (neutral leach residue) employ flotation for the recovery of silver and/or lead.

3. The reported success achieved at certain operations in flotation of ferrite residues (neutral leach), primarily for sphalerite recovery, suggests that flotation of neutral leach residues for lead and silver recovery merits consideration, particularly for those plants that cannot incorporate a high acid leach step.

3. FLOTATION OF NATURAL AND SYNTHETIC SILVER MINERALS - Binary System

The review of the literature indicated that there is relatively little information on the fundamental floatability of silver minerals such as could be expected to occur in zinc plant residues. Consequently, a series of flotation tests (10 min. roughing) was conducted with binary mixtures of various silver minerals (argentite, cerargyrite, native silver, tetrahedrite and chemically precipitated silver jarosite) and ground sand (65% minus 400 mesh, 13% minus 5 microns) to characterize the flotation behaviour of silver minerals under conditions potentially suitable for the treatment of zinc plant residues. The flotation parameters investigated were (i) pulp pH (3-9), (ii) collector, (iii) sulphidization (zero to 200% stoichiometric based upon Ag), (iv) sulphidization time (10-120 min.), and (v) silver mineral particle size (200/400 and minus 400 mesh).

In addition flotation tests were also carried out with (i) various silver-bearing jarosites, (ii) chemical equivalents of the silver-bearing minerals (Ag_2S and AgCl) prepared by precipitation under conditions simulating those encountered in zinc plant operations and (iii) silver-doped pyrite and sphalerite.

3.1 Sample Preparation and Characterization

The silver minerals (argentite, cerargyrite, native silver and tetrahedrite) were obtained from a mineral specimen dealer. The samples were washed with H_2O_2 before crushing and grinding to remove any surface contamination. The ground material was then screened (-200 +400 mesh, and -400 mesh) in methanol and stored at -15°C to minimize oxidation. The native silver was ground with silica sand to prevent the formation of lump-sized silver aggregates. The results of x-ray diffraction analysis and microscopic examination of the silver minerals are summarized in Table V, and the chemical assays are given in Table VI. The hand specimen of native silver had fine wire-type silver embedded within silicate material. The argentite sample was a well-formed crystalline specimen and assayed 84.8% Ag. The

TABLE V

X-RAY DIFFRACTION AND MICROSCOPIC ANALYSIS OF SILVER MINERALS

	X-Ray Diffraction	Microscopic
Native Silver	Major: silver metal silica	silver present as thin flakes caused in grinding, in minus 400 mesh fraction most of these flakes are ∿20μ
Argentite	Major: argentite	argentite is present in minus 400 mesh fraction in size of 20-30 microns, but some fines are also present
Cerargyrite	Major: cerargyrite cerussite Minor: silicates	Brown cerargyrite is predominant. Fine particles of cerussite (10-15%) Both minerals are fine <20 microns
Ag-Jarosite	Crystalline jarosite	very fine yellowish particles most finer than 5 microns
Tetrahedrite	Major: pyrite silicate gangue Minor: tetrahedrite	liberated pyrite and tetrahedrite

cerargyrite sample had dark brown color with waxy appearance. X-ray, microscopic and chemical analyses showed that the minus 400 mesh fraction cerargyrite contained 64.8% AgCl, 15% $PbSO_4$ and silicate material.

The chemically precipitated jarosite samples (Ag, Na-Ag, Pb-Ag jarosites)were supplied by CANMET and used as received in the binary flotation tests. The chemical analyses are given in Table VI.

Chemically precipitated equivalents of cerargyrite and argentite were prepared by reacting $AgNO_3$ with KCl and Na_2S, as precipitants, in neutral solution from C.E.Z. For the preparation of AgCl, KCl was dissolved in the zinc leach solution (110 gpL Zn, 3 gpL Fe and 15 gpL H_2SO_4) and, while stirring, an equivalent amount of $AgNO_3$ solution was added slowly and stirred for an additional 1 h. The reaction product was filtered and washed using hot distilled water. The Ag_2S was prepared similarly, except that prior to the Ag_2S precipitation, the neutral leach solution was treated to remove chloride ion. $AgNO_3$ was added to the chloride-free solution at 60°C, and Na_2S solution was then added slowly. The reaction was continued for 1 h before filtration and washing. The washed precipitates were dried under vacuum and stored at -15°C to minimize surface oxidation.

High purity crystalline mineral specimens of pyrite and sphalerite, ground to minus 400 mesh, were doped with silver by reaction with silver nitrate solution at pH 6.2. The minus 400 mesh samples were placed in flasks containing silver nitrate solution at 4.3×10^{-4} and 4.3×10^{-2} g Ag/g sample, and aged for 24 h with occasional shaking at room temperature. A change in color of mineral samples was observed as soon as the minerals were contacted with strong silver solution, especially for the sphalerite sample which changed from light yellow color to dark black within a few minutes. The reacted samples were filtered, washed with hot distilled water, and stored at -15°C.

TABLE VI

CHEMICAL ANALYSIS OF VARIOUS SILVER MINERALS

Sample	Size Fraction Mesh	Assay %						
		Ag	Pb	S_T	Cl	SO_4	Cu	Fe
Native silver	200/400 -400	42.4 8.01	0.018 0.047	0.18 0.27	-	-	-	-
Argentite	200/400 -400	84.8 83.3	0.13 0.083	12.5 12.9	-	-	-	-
Cerargyrite	200/400 -400	49.0 40.2	10.0 11.5	0.22 0.21	15.2 12.8	-	-	-
Tetrahedrite	200/400 -400	0.57 0.64	0.14 0.25	9.51 10.5	-	-	5.64 5.08	29.3 30.5
Silver jarosite	Chemical ppt	15.9	-	12.0	-	36.0	-	26.2
Na-Ag Jarosite	Chemical ppt	6.43	-	-	-	-	-	-
Pb-Ag Jarosite	Chemical ppt	1.86	9.23	-	-	-	-	-
Ag-Pb Jarosite	Chemical ppt	5.35	8.81	-	-	-	-	-

The results of chemical and x-ray diffraction analysis of the samples are given in Tables VII and VIII, respectively. The silver uptake by sphalerite at the two levels of silver addition was 100%, and that for pyrite was 100% at 4.3×10^{-4} g Ag/g pyrite and 82% at 4.3×10^{-2} g Ag/g pyrite.

Ground silica sand was used in the flotation tests as an inert matrix of the feed. The size analysis of the ground sand is given in Table IX.

3.2 Experimental Procedure

All flotation tests were carried out batch in a 250 g Denver flotation cell. The floatability of individual silver minerals was determined as a function of (i) pulp pH (3-9), (ii) collector, (iii) sulphidization time (10-120 min.), (iv) sulphide dosage (zero to 200% stoichiometric based upon Ag) and (v) silver mineral particle size (200/400 and minus 400 mesh). Experimentally, 250 g of ground sand, containing sufficient silver mineral to give the desired Ag level (generally 200-400 ppm) in the mixture, was slurried at 15% solids and conditioned for 5-min. at the specified pH. (The pH adjustment was done with H_2SO_4 or NaOH). The pulp was then conditioned for a further 5 min. with collector, and was floated with the addition of Aerofroth 65 (American Cyanamid Co.) for 10 min.

In sulphidization tests, sulphidization was carried out for 10-120 min. at the desired pH. For 10-min. sulphidization tests, the sodium sulphide solution was added once at the commencement of the sulphidization. In the prolonged sulphidization tests, the sulphide solution was added in stages throughout the sulphidization period.

Repeat tests (2-4) at a given flotation condition were carried out, and the average for these tests has been reported. Repeat tests showed some fluctuation in concentrate grade, but very little fluctuation in silver recovery or tails assay.

TABLE VII

CHEMICAL ANALYSES OF PRECIPITATED AND DOPED SAMPLES

Samples	Assays, %				
	Ag	Zn	Fe	S_T	Cl
Sphalerite					
undoped	0.002	65.5	0.35	32.8	-
4.3×10^{-4} g Ag/g	0.044	65.5	0.36	-	-
4.3×10^{-2} g Ag/g	4.28	62.4	0.43	-	-
Pyrite					
undoped	0.025	0.03	46.3	52.1	-
4.3×10^{-4} g Ag/g	0.079	-	46.2	-	-
4.3×10^{-2} g Ag/g	3.60	-	44.7	-	-
Ag_2S ppt	77.4	1.19	0.23	15.9	-
AgCl ppt	70.3	1.49	0.08	-	23.1

TABLE VIII

X-RAY DIFFRACTION AND MICROSCOPIC ANALYSIS OF PRECIPITATED AND DOPED SAMPLES

Sample	X-ray Diffraction	Microscopic Observation
AgCl ppt	well crystallized precipitate	pinkish white crystals, minus 20 microns
Ag_2S ppt	poorly crystallized, x-ray peaks are not sharp	very fine particles, black with metallic lustre, finer than 5 microns
Pyrite	almost pure pyrite no other peaks revealed	fine pyrite, no other minerals were observed ~20 microns
Sphalerite	sphalerite no other peaks	yellowish powder, very fine, less than 20 microns, very poor internal reflections indicating low Fe
Ag doped pyrite	no difference in lattice spacings or peak height	slightly darkened particle surface
Ag doped sphalerite	no difference in lattice spacings or peak height	completely darkened surface, transparent-like mineral became opaque after doping

TABLE IX

SIZE ANALYSES[1.] OF GROUND SAND

USED IN THE BINARY FLOTATION TESTS

Size Mesh or Microns	Sand[2.] wt %
+200	14.7
200/270	12.9
270/400	9.0
400/25	12.3
25/20	6.9
20/15	9.9
15/10	8.3
10/5	13.1
-5	12.9
Total	100.0

1. Hydrometer sedimentation method was used for sizing of minus 400 mesh.

2. Ground sand used in the binary system with silver minerals.

3.3 Results and Discussion

The initial series of silver flotation tests with physical mixtures of silver minerals and ground silica was carried out to investigate the floatability of various silver minerals as a function of pulp pH (pH 3-9), collector (amyl xanthate and dithiophosphate), particle size of silver minerals (minus 200 plus 400 mesh and minus 400 mesh), sulphidization time (10-60 min.) and dosage of sulphidizing agent. Most of the flotation tests were carried out under acidic conditions, since zinc plant leach residues are acidic and certain types may decompose under strongly alkaline conditions. Amyl xanthate, which is a powerful collector, was used in most tests, however, dithiophospate was also examined in acidic conditions in place of amyl xanthate, because of its better collecting power in acidic medium. In addition, anionic oxyhydryl collectors (oleic acid and alkyl sulphonate) were also examined for the flotation of silver jarosite.

3.3.1 Native Silver

The results of tests performed with native silver and ground silica sand are given in Table X. Pulp pH had no significant effect on silver flotation when using amyl xanthate. The silver recoveries ranged from 93.1 to 96.3%, giving rougher concentrates assaying 1426-1850 ppm Ag, from a feed at about 200 ppm Ag (tests 1-4). A short sulphidization (10 min.) with $Na_2S \cdot 9H_2O$ at 100 g/tonne did not affect the silver floatability at pH 3.0 or 8.0 (tests 16 and 17). However, silver recoveries tended to decrease with increasing sulphide dosage and sulphidization time at pH 3.0. At pH 8.0 the recovery was not affected by prolonged sulphidization. Concentrate grade tended to increase in tests with high sulphide dosage and long sulphidization time, indicating a low silica entrainment in the froth. Dithiophosphate was as effective as amyl xanthate at pH 5 (test 13).

TABLE X

FLOTATION TESTS[1] WITH ARTIFICIAL MIXTURES OF NATIVE SILVER AND GROUND SAND[2]

Test No.	pH	Amyl Xanthate g/T	Dithio-phosphate g/T	$Na_2S \cdot 9H_2O$ g/T	Stoichio-metric ratio of $S^{=}$ to Ag	Sulphidiza-tion time min.	Assays, ppm Ag			Ag Recovery in Conc. %
							Feed[3]	Concentrate	Tails	
1[4]	3.0	50	-	-	-	-	213	1850	15	93.5
2[4]	5.0	50	-	-	-	-	206	1532	16	93.1
3[4]	7.0	50	-	-	-	-	198	1604	10	95.5
4[4]	9.0	50	-	-	-	-	193	1426	8	96.3
13[4]	5.0	-	50	-	-	-	209	1557	9	96.2
16[4]	3.0	50	-	100	45	10	200	1512	14	93.2
17[4]	8.0	50	-	100	45	10	203	1446	17	92.9
43[4]	3.0	50	-	200	90	60	201	1590	15	93.4
32[4]	3.0	-	50	200	90	60	235	4514	27	89.9
22[4,6]	3.0	50	-	280	125	60	221	2220	31	86.3
33[4]	3.0	50	-	460	200	60	218	2303	36	84.9
61[4]	8.0	50	-	280	125	60	185	2245	15	92.5
62[5]	5.0	50	-	100	15	10	592	13,550	19	96.9
56[5]	3.0	50	-	-	-	-	577	9180	21	96.6
86[5]	5.0	50	-	500	25	10	1497	38,316	77	95.0
83[5]	3.0	50	-	-	-	-	1481	27,615	69	95.6

1. 250 g of ground sand and silver minerals were slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Ground sand - 65% minus 400 mesh, 13% minus 5 microns.

3. Feed assays were calculated from the assays and weights of the products.

4. -400 mesh native silver.

5. 200/400 mesh native silver.

6. Average of three tests.

The tests with -200 +400 mesh native silver, at two pH levels with and without sulphidization, show that there was no basic floatability difference between this size fraction and the minus 400 mesh fraction. However, the coarse native silver fraction floated relatively fast as compared to the tests with the fine fraction, resulting in high grade concentrates with high concentration ratios. It seems that a small dose of sulphide in tests with coarse particles may have promoted the flotation of native silver, or suppressed the flotation of silica particles, without affecting the tails assays (tests 62-66 and 83-86). Although there was no effect on recovery, high silver containing heads produced high silver tails at a given flotation condition.

3.3.2 Cerargyrite

The results of flotation tests with cerargyrite are given in Table XI. Flotation with amyl xanthate at pH 3-9, resulted in silver recoveries of 95.2-98.7%, with the highest recovery being achieved at pH 7.0. Dithiophosphate was as effective as amyl xanthate in a comparison test conducted at pH 5.0.

Sulphidization tests, with 15-90% stoichiometric Na_2S addition and 10-120 min. sulphidization time at pH 3.0 and 8.0, showed that the floatability of cerargyrite was not affected within the range examined. As shown in the table, sulphidization tests produced cencentrates with somewhat higher silver assays. Furthermore, prolonged sulphidization resulted in generally increased concentration ratios. These results indicate that sulphidization prior to flotation enhances the flotation of cerargyrite and reduces the entrainment of silica in the froth. A test (No. 56) with kerosene alone as collector gave a silver concentrate assaying 2154 ppm Ag with 56.9% recovery after sulphidization.

Coarse (-200 +400 mesh) cerargyrite flotation tests with about 600 ppm Ag in the feed at pH 3 and 5, with and without sulphidization, respectively, gave concentrates assaying 8208-8693 ppm Ag with recoveries

TABLE XI

FLOTATION TESTS[1] WITH ARTIFICIAL MIXTURES OF CERARGYRITE AND GROUND SAND[2]

Test No.	pH	Amyl Xanthate g/T	Dithio-phosphate g/T	$Na_2S \cdot 9H_2O$ g/T	Stoichio-metric ratio of $S^{=}$ to Ag	Sulphidiza-tion time min.	Assays, ppm Ag			Ag Recovery in Conc. %
							Feed[3]	Concentrate	Tails	
5[4]	3.0	50	-	-	-	-	524	4163	19	96.7
6[4]	5.0	50	-	-	-	-	525	3736	29	95.2
7[4]	7.0	50	-	-	-	-	512	4288	7	98.7
8[4,7]	9.0	50	-	-	-	-	528	8001	20	96.5
14[4,7]	5.0	-	50	-	-	-	563	5053	15	97.8
18[4,7]	3.0	50	-	100	16	10	538	5803	22	96.3
19[4,7]	8.0	50	-	100	16	10	516	4504	10	98.2
23[4,8]	3.0	50	-	280	45	60	555	7009	37	93.9
39[4]	3.0	50	-	570	90	60	560	7052	25	95.9
40[4]	3.0	50	-	570	90	120	525	6745	21	93.8
41[4]	3.0	-	50	280	45	60	574	9203	26	95.7
42[4]	3.0	-	50	570	90	60	550	6880	19	96.8
55[4]	8.0	50	-	570	90	60	527	5209	36	93.8
56[5]	8.0	-	-	570	90	60	520	2154	260	56.9
64[6]	5.0	50	-	100	15	10	577	8207	16	97.4
67[6]	3.0	50	-	-	-	-	654	8693	12	98.3
87[6]	5.0	50	-	500	25	10	3897	23,050	306	93.4
85[6]	3.0	50	-		-	-	3913	[illegible],985	367	91.1

1. 250 g of ground sand and silver minerals were slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65. In sulphidization tests, sulphidization was done at the given pH before adding collector.
2. Ground sand - 65% minus 400 mesh, 13% minus 5 microns.
3. Feed assays were calculated from the assays and weights of the products.
4. -400 mesh cerargyrite
5. -400 mesh cerargyrite - kerosene
6. 200/400 mesh cerargyrite
7. Average of two tests
8. Average of four tests.

of 97.4-98.3% (tests 64 and 67). The tails assayed 16 and 12 ppm Ag. These results show that the floatability of cerargyrite is not affected by particle size in the range from minus 200 mesh to a few microns.

Another set of tests similar to tests 64 and 67 was carried out with feed assaying about 3900 ppm Ag to examine the flotation behaviour of a high grade feed (tests 85 and 87). Although high grade concentrates were produced, the silver recoveries were reduced to 91.1-93.4%, and the tails assayed 306-367 ppm Ag. The exact causes for the reduced recovery and high tails are not known, however, reagent deficiency in the pulp could be the main factor.

3.3.3 Argentite

In Table XII, the results of flotation tests with argentite are shown. Similar to the above two silver minerals, flotation at pH 3-9 using amyl xanthate produced 10 min. rougher concentrates assaying 4560-5817 ppm Ag with recoveries of 96.6-97.9% from a feed of about 570 ppm Ag. The tails assayed 13-23 ppm Ag (tests 9-12). A test (No.15) with dithiophosphate gave a concentrate assaying 7384 ppm Ag with recovery of 96.6% at pH 5.0, indicating a better selectivity than amyl xanthate.

Short sulphidization tests at pH 3.0 and 8.0 with 100 g/tonne $Na_2S \cdot 9H_2O$ showed no significant effect on argentite flotation at pH 8.0 when using amyl xanthate as collector, and a very slight decrease in recovery at pH 3.0 (tests 20 and 21). Prolonged sulphidization with 45-90% stoichiometric addition of $Na_2S \cdot 9H_2O$ at pH 3.0 and 7.0 showed no significant decrease in silver recovery with amyl xanthate. Similarly, sulphidization and flotation with dithiophosphate gave concentrates assaying 5637-8154 ppm Ag with recoveries of 94.4-97.8%. The results of tests with minus 200 plus 400 mesh argentite at pH 3 and 5, with and without sulphidization, show that the coarse argentite floated without any difficulty, giving silver recoveries 98.8-99.1%

TABLE XII

FLOTATION TESTS[1] WITH ARTIFICIAL MIXTURES OF ARGENTITE AND GROUND SAND[2]

Test No.	pH	Amyl Xanthate g/T	Dithiophosphate g/T	$Na_2S \cdot 9H_2O$ g/T	Stoichiometric ratio of $S^{=}$ to Ag	Sulphidization time min.	Assays, ppm Ag			Ag Recovery in Conc. %
							Feed[3]	Concentrate	Tails	
9[4]	3.0	50	-	-	-	-	558	5817	13	97.9
10[4]	5.0	50	-	-	-	-	611	5022	23	96.7
11[4]	7.0	50	-	-	-	-	553	4567	21	96.6
12[4]	9.0	50	-	-	-	-	605	5354	18	97.4
15[4,6]	5.0	-	50	-	-	-	573	7383	16	96.6
20[4]	3.0	50	-	100	16	10	593	5638	37	94.3
21[4,7]	8.0	50	-	100	16	10	505	5403	17	97.0
24[4,6]	3.0	50	-	280	45	60	561	6611	13	97.9
35[4]	3.0	50	-	570	90	60	597	6600	28	95.7
63[4]	7.0	50	-	570	90	60	535	8224	34	94.0
36[4]	3.0	-	50	160	25	60	548	7124	33	94.4
44[4]	3.0	-	50	280	45	60	672	5637	17	97.8
37[4]	3.0	-	50	570	90	60	569	8154	16	97.4
65[5]	5.0	50	-	100	16	10	656	12,569	8	98.8
68[5]	3.0	50	-	-	-	-	651	8,902	6	99.1
88[5]	5.0	50	-	500	25	10	3422	87,093	140	96.0
84[5]	3.0	50	-	-	-	-	3486	63,208	307	91.6

1. 250 g of ground sand and silver minerals were slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65. In sulphidization tests, sulphidization was done at the given pH before adding collector.
2. Ground sand - 65% minua 400 mesh, 13% minus 5 microns.
3. Feed assays were calculated from the assays and weights of the products.
4. -400 mesh argentite
5. 200/400 mesh argentite
6. Average of three tests
7. Average of two tests

from a feed of about 650 ppm Ag. The tails assayed 6-8 ppm Ag. Other tests with a feed containing about 3500 ppm Ag resulted in concentrates assaying 63,208-87,093 ppm Ag with recoveries of 91.6-96.7%. However, the tails assayed 140-307 ppm Ag. (This suggests that although coarse argentite is readily floatable, a light sulphidization could be beneficial to increase the concentrate grade as well as the silver recovery). The high silver tails could be due to reagent deficiency in the pulp when bulk of the silver was removed in the froth or high grade feed may require a longer conditioning time.

In general, the above results show that argentite is readily floatable, with or without sulphidization, under the range of conditions examined, giving silver recoveries of 94-99%.

3.3.4 Tetrahedrite

Results of flotation tests with tetrahedrite are given in Table XIII. A test (No. 76) at pH 3.0 with amyl xanthate resulted in a 10-min. rougher concentrate assaying 1182 ppm Ag witn 94.5% silver recovery. At pH 7.0, the concentrate grade increased to 1546 ppm Ag, at 93.8% recovery.

Sulphidization (100-570 g/tonne $Na_2S \cdot 9H_2O$) at pH 3.0 with minus 400 mesh tetrahedrite did not affect the flotation, giving concentrates assaying 1158-1205 ppm Ag with recoveries of 92.5-93.4% (tests 73 and 74). Sulphidization-flotation of the minus 200 plus 400 mesh fraction at pH 3.0 produced a concentrate assaying 2332 ppm at 89.8% recovery.

3.3.5 Silver Jarosite

A series of flotation tests with chemically precipitated silver jarosite at pulp pH 3-9 using various collectors (xanthate, dithiophosphate, kerosene, oleic acid and alkyl sulphonate), with and without sulphidization, was carried out. The silver content in the heads was varied from 600-3000 ppm Ag. The dosage of collector was 50 g/tonne for amyl xanthate and

TABLE XIII

FLOTATION TESTS[1] WITH TETRAHEDRITE/SAND MIXTURES

Test No.	Pulp pH	Reagent, g/t		Stoichiometric Ratio of $S^{=}$ to Ag	Sulphidization time min.	Assays, ppm Ag			Ag Recovery in Conc. %
		Amyl Xanthate	$Na_2S \cdot 9H_2O$			Feed[2]	Concentrate	Tails	
76[3]	3.0.	50	-	-	-	186	1,182	26	94.5
77[3]	7.0	50	-	-	-	160	1,546	11	93.8
74[3]	3.0	50	100	65	10	171	1,205	13	93.4
73[3]	3.0	50	570	330	60	152	1,158	13	92.5
75[4]	3.0	50	100	65	10	256	2,332	29	89.8

1. 250 g of ground sand and silver mineral were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was then further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65.

2. Feed assays calculated from the assays and weights of the products.

3. Minus 400 mesh.

4. Minus 200 mesh plus 400 mesh.

dithiophosphate, and 400 g/tonne for kerosene, oleic acid and petroleum sulphonate. The results are given in Table XIV. The tests with conventional sulphide collectors, with and without sulphidization, at pH 3-9 resulted in a very poor floatability of precipitated silver jarosite. Without sulphidization, recoveries increased from 15% at pH 3.0 (primarily mechanical entrainment) to 39-42% at pH 7-9. Sulphidization with varying dosages $Na_2S \cdot 9H_2O$ had no effect on silver jarosite floatability at pH 3.0, and no improvement was obtained with prolonged sulphidization or operation at higher pH. These results clearly indicate that the conventional sulphide flotation schemes are not applicable to the flotation of silver jarosite.

Flotation of silver jarosite with anionic oxhydryl collectors resulted in very high silver recoveries. The oleic acid flotation at pH 4-8 produced concentrates assaying 4,356-20,578 ppm Ag with recoveries 97.7-99.5% from heads containing 1800-2000 ppm Ag. Although the silver recovery was over 99% at pH 6 and 8, the concentrate grade was low due to the co-flotation of silica in this pH range. (It should be noted that quartz should not float at neutral or alkaline pH with fatty acid collector unless there exists a specific activation of quartz by heavy metal ions. It is possible that certain cations in jarosite were released at alkaline pH which caused the quartz activation). The rougher concentrate weights were 80.9% and 28.2% of the feed for pH 6 and 8, respectively, while the test at pH 4.0 gave only 9.5% of the feed weight.

Tests (Nos. 157,158) with sulphonate-type anionic collector showed that neutral alkaline pH was favourable for the flotation of silver jarosite. At pH 6.0 and 9.0, concentrates assaying 26,610-31,995 ppm Ag were produced with recoveries of about 90% from a feed containing 3000 ppm Ag. The tails assayed 320-340 ppm Ag. There was no significant co-flotation of silica at pH 6-9 in contrast to the tests with oleic acid. The difference with these two anionic collectors acting on quartz particles could be due to the difference in chemical and physical affinity of the collectors for the mineral surfaces. Although not shown in the table,

TABLE XIV

FLOTATION TESTS[1] WITH ARTIFICIAL MIXTURES OF SILVER JAROSITE AND GROUND SAND[2]

Test No.	pH	Amyl Xanthate g/T	Dithio-phosphate g/T	Other Reagent g/T	$Na_2S \cdot 9H_2O$ g/T	Stoichio-metric Ratio of $S^{=}$ to Ag	Sulphidiza-tion time min.	Assays, ppm Ag			Ag Recovery in Conc. %
								Feed[3]	Concentrate	Tails	
50	3.0	50	-	-	-	-	-	636	844	610	15.0
51	5.0	50	-	-	-	-	-	510	1441	400	29.9
52	7.0	50	-	-	-	-	-	612	2198	400	42.3
53	9.0	50	-	-	-	-	-	567	2247	380	39.7
54	5.0	-	50	-	-	-	-	601	1671	480	28.4
48[4]	3.0	50	-	-	100	15	10	607	1204	550	17.4
60	3.0	50	-	-	100	15	10	586	771	570	10.5
49	8.0	50	-	-	100	15	10	646	2077	490	31.6
47	3.0	50	-	-	340	50	60	622	801	600	12.7
46	3.0	50	-	-	680	100	60	582	820	560	13.2
45	3.0	50	-	-	680	100	120	625	952	590	14.8
57	7.0	50	-	-	680	100	60	600	1548	500	24.5
58	7.0	-	50	-	680	100	60	611	992	580	12.2
59	7.0	-	-	Kerosene	680	100	60	592	1191	540	16.2
80	4.0	-	-	Oleic acid	-	-	-	2007	20,578	52	97.7
81	6.0	-	-	Oleic acid	-	-	-	1793	4356	16	99.5
82	8.0	-	-	Oleic acid	-	-	-	1923	6770	24	99.1
157	6.0	-	-	Sulphonate	-	-	-	3032	26,610	320	90.5
158	9.0	-	-	Sulphonate	-	-	-	2954	31,995	340	89.5

1. 250 g of ground sand and silver minerals were slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Ground sand - 65% minus 400 mesh, 13% minus 5 microns.

3. Feed assays were calculated from the assays and weights of the products.

4. Average of two tests.

flotation tests at pH lower than 4.0 gave very poor silver jarosite flotation. This indicates that in acidic conditions there is no collector adsorption on either mineral surface. In addition to the tests performed with pure silver-jarosite, a set of tests was also carried out using Ag-Na and Ag-Pb jarosite samples to explore the flotation response in the mildly acidic region using anionic oxhydryl collectors. The results are given in Table XV.

The silver-sodium jarosite floated with about 90% recovery at pH 6.3 when sulphonate was used as collector. However, at pH 3.3 and with sodium oleate, the silver recovery was only 17.5. On the other hand, the high-silver Ag-Pb jarosite floated at pH 3.4-6.3, with either collector giving over 95% silver recovery.

3.3.6 Precipitated Silver Sulphide and Silver Chloride

The flotation results with chemical equivalents of argentite and cerargyrite, prepared by precipitation from zinc plant leach solution are given in Table XVI. The precipitated silver sulphide and silver chloride floated readily, giving over 97% silver recovery at pH 3 and pH 5 to a 10-min. rougher concentrate. Sulphidization with 860 g/t $Na_2S \cdot 9H_2O$ (55-62% stoichiometric) for 10-60 min. did not affect the floatability.

Microscopic examination of the two precipitates used in flotation showed them to be less than 5 microns, and mostly submicron. The naturally occurring silver sulphide and silver chloride minerals tested previously were ground to minus 400 mesh (37 microns). Thus, the results of these flotation tests with chemical precipitates (Ag_2S and AgCl) and their naturally occurring analogues indicate that the floatabilities are not affected by the particle size.

3.3.7 Silver-Doped Pyrite and Sphalerite

The flotation recoveries of undoped pyrite and sphalerite and silver-doped pyrite and sphalerite were examined, with and without sulphidization, over the pH range 3-10. The natural pyrite floated with

TABLE XV

FLOTATION TESTS[1] WITH ARTIFICIAL MIXTURES OF SILVER-BEARING JAROSITES AND GROUND SAND[2]

Test No.	Pulp pH	Collector, g/T		Assays, %			Ag recovery in conc. %	Conc. wt %
		Na-oleate	Alkyl Sulphonate	Feed[3]	Concentrate	Tails		
(a) Ag-Na Jarosite (6.43% Ag)								
209	3.3	400	-	0.172	0.356	0.155	17.5	8.4
210	6.3	-	200	0.175	0.999	0.021	89.8	15.7
(b) Ag-Pb Jarosite (6.35% Ag, 8.81 % Pb)								
212	3.4	400	-	0.193	1.337	0.009	95.9	14.1
211	6.3	-	200	0.195	0.891	0.011	95.6	21.0
(c) Pb-Ag Jarosite (1.86% Ag, 9.33% Pb)								
214	3.0	400	-	0.146	0.551	0.04	78.2	20.7
213	6.3	-	200	0.144	0.627	0.022	87.9	20.3

1. 250 g of ground sand and silver-containing jarosite were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65.

2. Ground sand: 65% minus 400 mesh, 13% minus 5 microns.

3. Feed assays were calculated from the assays and weights of the products.

TABLE XVI

FLOTATION RESULTS[1] OF Ag_2S AND AgCl PRECIPITATES[2] MIXED WITH GROUND SAND

Test No.	pH	$Na_2S \cdot 9H_2O$ g/T	Stoichiometric ratio of S to Ag %	Sulphidization time, min.	Assays, % Ag			Ag Recovery in conc. %
					Feed[4]	Concentrate	Tails	
Ag_2S Precipitate								
148	3.0	-	-	-	0.140	3.438	0.0035	97.6
149	5.0	-	-	-	0.136	3.092	0.0038	97.3
150	3.0	200	12	10	0.144	3.415	0.0049	96.7
151	5.0	200	12	60	0.146	4.159	0.0038	97.5
AgCl Precipitate								
152	3.0	-	-	-	0.121	2.985	0.0017	98.7
153	5.0	-	-	-	0.117	2.503	0.0034	97.2
154	3.0	200	13	10	0.126	3.306	0.0040	96.9
155	5.0	200	13	60	0.128	2.973	0.0029	97.8

1. 250 g of ground sand and precipitates were slurried at 15% solids, and conditioned at the specific pH for 5-min. The pulp was further conditioned for 5-min.with 50 g/t amyl xanthate. Rougher flotation was conducted for 10-min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Ag_2S and AgCl were precipitated in a zinc leach solution (120 g/L Zn, 4.2 g/L Fe).

3. Ground sand: 65% minus 400 mesh, 13% minus 5 microns.

4. Feed assays were calculated from the assays and weights of the products.

95.6% recovery at pH 3 and 83.4% at pH 7 (Table XVII). The pyrite recovery was reduced after sulphidization to 83.8% at pH 3 and 64.4% at pH 7. The depression mechanism of sodium sulphide on pyrite is not known, but an electrokinetic study([61]) has shown that the pyrite surface becomes positively charged in the acidic pH region. This positive surface charge could induce the adsorption of xanthate anions. In recent years, the chemistry of pyrite flotation has been given with reference to the mechanisms of collection and depression([62,63]). Whatever the collector mechanism in the flotation of pyrite, reagents such as cyanide, hydroxide sulphite and sulphide anions are being used for the depression of pyrite. However, the results of flotation with silver-doped pyrite show that the floatability of the treated pyrite was not affected by pH or sulphidization within the range of conditions examined, giving iron (pyrite) recoveries of 91-96%. The mechanism of copper activation of pyrite and pyrrhotite have been discussed([64,65]) and it was postulated that the activation reaction of pyrite with copper could be written as

$$FeS_2 + Cu^{++} \rightarrow CuS + S^{\circ} + Fe^{++}$$

However, no reference could be found in the literature concerning the activation of pyrite with silver or other heavy metal ions.

For the case of sphalerite, as shown in Table XVIII, the tests with natural sphalerite gave recoveries of 96.9-98.4% at pH 3, with and without sulphidization. At pH 7, without sulphidization, the zinc recovery was 92.3%. On the other hand, with sulphidization, the zinc recovery was reduced to 28.7%, and at pH 10, the natural pH with the sodium sulphide additions, only 10.4% of the zinc was floated. The silver-doped sphalerite showed similar flotation characteristics, giving low recoveries at higher pH and with sulphidization.

TABLE XVII

FLOTATION[1] OF PYRITE AND SILVER-DOPED PYRITE MIXED WITH GROUND SAND[2]

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/T	Sulphidization time, min.	Assays, %						Recovery, %	
				Feed		Concentrate		Tails			
				Ag	Fe	Ag	Fe	Ag	Fe	Ag	Fe
Undoped Pyrite,(200 ppm Ag)											
122	3.0	-	-	-	0.856	-	16.7	-	0.038	-	95.6
123	7.0	-	-	-	0.961	-	12.1	-	0.17	-	83.4
134	3.0	1500	10	-	0.907	-	9.20	-	0.16	-	83.8
170	7.0	1500	10	-	0.912	-	13.1	-	0.34	-	64.4
135	10.0	1500	10	-	0.910	-	17.6	-	0.23	-	75.7
Doped Pyrite (4.3×10^{-4} g Ag/g pyrite, 820 ppm Ag)											
126	3.0	-	-	-	0.698	-	12.9	-	0.024	-	96.7
127	7.0	-	-	-	0.674	-	11.3	-	0.063	-	91.1
138	3.0	1500	10	-	0.644	-	12.3	-	0.033	-	95.1
169	7.0	1500	10	-	0.822	-	15.6	-	0.034	-	96.1
139	10.0	1500	10	-	0.661	-	12.3	-	0.085	-	87.8
Doped Pyrite (4.3×10^{-2} g Ag/g pyrite, 3.79% Ag)											
130	3.0	-	-	0.056	0.709	1.013	12.4	0.0031	<0.05	94.8	92.8
131	7.0	-	-	0.056	0.681	1.320	15.4	0.0024	<0.05	95.9	92.7
144	3.0	1500	10	0.051	0.632	0.799	9.71	0.003	<0.05	95.0	92.3
147	3.0	1500	10	0.051	0.646	0.890	11.3	0.004	<0.05	92.5	92.2
146	7.0	1500	10	0.054	0.645	1.136	13.6	0.004	<0.05	92.8	92.2

1. 250 g of ground sand and pyrite were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was further conditioned for 5 min. with 50 g/t amyl xanthate. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.
2. Ground sand: 65% minus 400 mesh, 13% minus 5 microns.
3. Feed assays were calculated from the assays and weights of the products.

TABLE XVIII

FLOTATION[1] OF SPHALERITE AND SILVER-DOPED SPHALERITE MIXED WITH GROUND SAND[2]

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/T	Sulphidization time, min. %	Assays, %						Recovery, %	
				Feed		Concentrate		Tails			
				Ag	Zn	Ag	Zn	Ag	Zn	Ag	Zn
Undoped Sphalerite (20 ppm Ag)											
125	3.0	-	-	-	1.332	-	20.3	-	0.023	-	98.4
124	7.0	-	-	-	1.239	-	22.8	-	0.10	-	92.3
136	3.0	1500	10	-	1.353	-	26.9	-	0.043	-	96.9
171	7.0	1500	10	-	1.3.8	-	10.3	-	0.97	-	28.7
137	10.0	1500	10	-	1.363	-	3.08	-	1.28	-	10.4
Doped Sphalerite (4.3×10^{-4} g Ag/g sphalerite, 460 ppm Ag)											
128	3.0	-	-	-	1.053	-	24.5	-	0.031	-	97.2
129	7.0	-	-	-	1.056	-	22.7	-	0.059	-	94.6
140	3.0	1500	10	-	1.033	-	34.0	-	0.065	-	93.9
172	7.0	1500	10	-	1.110	-	6.21	-	0.88	-	24.1
141	10.0	1500	10	-	1.058	-	2.53	-	1.02	-	6.1
Doped Sphalerite (4.3×10^{-2} g Ag/g sphalerite, 4.34% Ag)											
133	3.0	-	-	0.071	1.050	1.444	21.3	0.0019	0.03	97.4	97.3
142	3.0	1500	10	0.0626	1.030	1.325	23.5	0.0074	0.047	88.7	95.6
145	7.0	1500	10	0.0655	1.013	0.737	14.6	0.023	0.15	67.0	86.1
173	10.0	1500	10	0.0682	0.897	0.319	6.66	0.057	0.64	20.0	31.7

1. 250 g of ground sand and sphalerite were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was further condtioned for 5 min. with 50 g/t amyl xanthate. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Ground sand: 65% minus 400 mesh, 13% minus 5 microns.

3. Feed assays were calculated from the assays and weights of the products.

There are numerous publications dealing with the activation of sphalerite by copper ions. Recently, a comprehensive review of the sphalerite activation has been published([66]). For copper activation, it is well established that the sphalerite surface undergoes an 1:1 Cu/Zn exchange reaction([67]). Copper uptake by sphalerite proceeds very rapidly, initially to form several monolayers within a few minutes, and then continues very much more slowly. The activation of sphalerite by ions other than copper has also been studied ([68-70]). They found that the uptake of silver by sphalerite is an exchange reaction which continues indefinitely.

As mentioned in a previous section of this report, when the creamy light-colored sphalerite sample was treated with a solution containing 4.3×10^{-2} g Ag/g sphalerite, an instantaneous darkening of the surface was observed. Also solution analyses revealed that two silver ions were replaced by one zinc ion, suggesting a chemical reaction such as

$$ZnS + 2Ag^{+} \rightarrow Ag_2S + Zn^{++}$$

This type of reaction could be controlled by the ratio of solubility products of metal sulphides involved, and, as reference, the solubility products of various relevant metal compounds are given in Table XIX.

The form of silver coating on the sphalerite is not definitely known. X-ray diffraction data obtained with the clean and the doped sphalerite showed no difference in the lattice spacings, which agrees with published data([69]), suggesting that the silver coating may be amorphous Ag_2S.

It is apparent from published work that the mechanism of the reaction of sphalerite with Ag^{+} is entirely different from that with Cu^{++}. Furthermore, the flotation characteristics of the silver-doped

TABLE XIX

SOLUBILITY PRODUCT OF METAL COMPOUNDS[62,66,71,72]

Anionic Species	Metallic ions					
	Zn^{++}	Cu^{++}	Ag^{+}	Pb^{++}	Cu^{+}	Fe^{++}
Ethyl Xanthate	4.9×10^{-9}	-	5.0×10^{-19}	1.7×10^{-17}	5.2×10^{-20}	17.9×10^{-8}
Ethyldithiophosphate	1.5×10^{-2}	1.4×10^{-16}	1.5×10^{-16}	7.5×10^{-12}	-	-
Sulphide	2.6×10^{-26}	4×10^{-36}	6.3×10^{-52}	3.4×10^{-28}	8.0×10^{-49}	2.5×10^{-19}
Hydroxide	1.62×10^{-17}	1.2×10^{-20}	1.52×10^{-8}	8.1×10^{-17}	2.0×10^{-15}	1.8×10^{-15}
Chloride	-	-	1.5×10^{-10}	-	-	-

pyrite and sphalerite, as shown in the tables, are quite different, which indicates the reaction products on the pyrite and sphalerite surface may not be the same species. An extensive literature search revealed that, although there are publications about the activation and deactivation of sphalerite, there are no references to the flotation of silver-activated sphalerite or pyrite. More work in this direction is warranted in order to understand the flotation properties and the mechanism of silver activation of sphalerite and pyrite that may be present in zinc hydrometallurgical circuits.

3.4 Conclusions

Flotation tests with binary mixtures of natural silver minerals (argentite, native silver, cerargyrite and tetrahedrite), synthetic silver minerals (chemically precipitated silver jarosites, silver sulphide and silver chloride), and silver-doped pyrite and sphalerite have shown that, with the exception of the silver jarosites, all the silver minerals and compounds can be readily floated with high recovery in acid media using sulphide collectors. Specifically:

(i) argentite, cerargyrite, native silver and tetrahedrite were readily floated in the sand mixture without sulphidization, giving 92-99% recovery. Sulphidization of argentite and cerargyrite did not affect the silver recoveries, but prolonged sulphidization of native silver at over 100% stoichiometric sulphide addition reduced silver recovery by 5-10%.

(ii) the flotation of chemically precipitated silver jarosite with the conventional sulphide collectors was not feasible.

(iii) anionic oxhydryl collectors such as oleic acid and petroleum sulphonate for silver jarosite flotation gave 90-99% silver recovery under neutral or mildly alkaline conditions, but co-flotation of silica was highly reduced

when sulphonate was used instead of oleic acid in the binary mixture.

(iv) flotation tests using chemically precipitated Ag_2S and AgCl showed that the floatabilities of the samples were not affected by sulphidization (860 g/t $Na_2S \cdot 9H_2O$ equivalent to 55-62% stoichiometric ratio of $S^=$ to Ag^+) of 10-60 min. in acidic pH. Silver recoveries of over 97% were obtained with 50 g/t amyl xanthate.

(v) comparative flotation tests using pyrite, sphalerite and silver-doped pyrite and sphalerite have shown that the silver-doped minerals had high floatabilities (over 95% recovery) in acidic pulps, with and without sulphidization.

(vi) the mechanisms of silver activation of pyrite and sphalerite are radically different, and more work is warranted to understand the flotation and activation mechanisms of these sulphide minerals.

4. FLOTATION OF NATURAL AND SYNTHETIC SILVER MINERALS - Tertiary System

A series of flotation tests using a three-component system (about 40% minus 5 microns) prepared with ground silica, silver mineral (cerargyrite and silver jarosite) and slimes (hematite, goethite and ammonium jarosite) was carried out at pH 3 and pH 8. The purpose of the investigation was to evaluate the effect of slimes such as might occur in zinc plant leach residues.

4.1 Sample Preparation and Characterization

The cerargyrite and pure silver jarosite samples used were those described previously in the binary flotation study. The hematite sample was supplied by Canadian Electrolytic Zinc, from a pilot plant operation of a

proprietary process. The goethite sample was obtained from Vieille Montagne, and the ammonium jarosite was prepared and supplied by CANMET. The physical and chemical characteristics of the above samples are given in Table XX, and the size analyis of the ground sand is given in Table XXI.

The actual size distribution of the sand/slimes mixture used in the tertiary system was 93, 95 and 84% minus 400 mesh for hematite, goethite and ammonium jarosite mixtures, respectively.

4.2 Experimental Procedure

All the flotation tests were carried out in a 250 g Denver flotation cell. Experimentally, 200 g of ground sand, 50 g of slimes and the silver mineral were slurried with various dispersants (starch, water glass, and sodium phosphate) at about 15% solids and conditioned for 5 min. at the specified pH. The pulp was then conditioned for a further 5 min. with collector, and was floated with the addition of Aerofroth 65 (American Cyanamid Co.) for 10 min.

4.3 Results and Discussion

4.3.1 Cerargyrite/Sand/Slimes Mixture

A series of flotation tests with hematite, ammonium jarosite and goethite, and ground sand admixed with cerargyrite was carried out at pH 3 and 8 with various slime dispersants. Amyl xanthate and diphenylguanidine were used as collectors. The test results are given in Table XXII.

Without dispersant at pH 3.0, rougher silver recoveries when floating with xanthate were 69.1, 86.5 and 76.6% for mixtures containing hematite, ammonium jarosite and goethite, respectively, compared to 96.7% recovery without slimes. The use of dispersants with xanthate at pH 3.0 had little effect on recovery or concentrate grade, but increasing the pH to 8 resulted in a slight improvement in silver recovery. Silver

TABLE XX

CHARACTERISTICS OF HEMATITE, GOETHITE AND AMMONIUM JAROSITE SLIMES

	Assays %	X-ray Diffraction	Microscopic Examination
Hematite 83% minus 400 mesh	Ag : 0.028 Fe : 45.4 Pb : 1.09 Zn : 1.83	major : hematite with low crystallinity minor : silica zinc ferrite anglesite	hematite is very fine (<1 μ), aggregates of fines, coarse ferrite and silica up to 100 μ, dark red powder
Goethite 92% minus 400 mesh	Ag : 0.013 Fe : 37.1	major : poorly crystallized goethite minor : jarosite and small amount of gypsum and silicate	mostly fine goethite, coarse silicate and ferrite, dark brown powder
Ammonium Jarosite 74% minus 200 mesh, 38% minus 400 mesh	Fe : 30.9	well crystallized jarosite	mixture of fines (<1 μ) and aggregates

TABLE XXI

SIZE ANALYSES[1.] OF GROUND SAND
USED IN THE TERTIARY FLOTATION TESTS

Size Mesh or Microns	Sand[2.] wt %
+200	0.6
200/270	4.1
270/400	1.4
400/25	10.8
25/20	7.4
20/15	11.1
15/10	12.3
10/5	20.8
-5	31.5

1. Hydrometer sedimentation method was used for sizing of minus 400 mesh.

2. Ground sand used in the tertiary system with silver minerals and and residue slimes.

TABLE XXII

FLOTATION TESTS[1] WITH CERARGYRITE/SAND/SLIMES MIXTURES

Test No.	pH	Dispersant		Collectors		Assays ppm Ag			Ag Recovery in Conc. %	Slimes Phase[4]
		Name	g/T	Name	g/T	Feed[2]	Concentrate	Tails		
5	3.0	-	-	Amyl Xanthate	50	524	4163	19	96.7	-
93	3.0	-	-	Amyl Xanthate	50	708	10,698	229	69.1	Hematite
94	3.0	Starch	100	Amyl Xanthate	50	707	11,919	202	72.7	Hematite
95	3.0	Na_2SiO_3	400	Amyl Xanthate	50	663	9873	213	69.4	Hematite
99	8.0	Na_2SiO_3	400	Amyl Xanthate	50	716	11,564	158	79.0	Hematite
100	8.0	$(NaPO_4)_6$	400	DPG[3]	480	713	9160	57	92.6	Hematite
118	3.0	$(NaPO_4)_6$	400	DPG[3]	480	682	10,572	95	86.9	Hematite
96	3.0	-	-	Amyl Xanthate	50	634	9840	91	86.5	NH_4 Jarosite
97	3.0	Starch	100	Amyl Xanthate	50	642	8081	53	92.3	NH_4 Jarosite
98	3.0	Na_2SiO_3	400	Amyl Xanthate	50	565	12,268	91	84.5	NH_4 Jarosite
103	8.0	Na_2SiO_3	400	Amyl Xanthate	50	646	11,061	28	95.9	NH_4 Jarosite
104	8.0	$(NaPO_4)_6$	400	DPG[3]	480	606	3793	69	90.3	NH_4 Jarosite
119	3.0	$(NaPO_4)_6$	400	DPG[3]	480	616	9284	47	92.8	NH_4 Jarosite
112	3.0	-	-	Amyl Xanthate	50	669	7317	168	76.6	Goethite
113	3.0	$(NaPO_4)_6$	400	Amyl Xanthate	50	633	7105	129	81.1	Goethite
116	8.0	$(NaPO_4)_6$	400	Amyl Xanthate	50	656	7334	89	87.5	Goethite

1. 200 g of ground sand, 50 g of zinc leach residue slimes and silver mineral were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was then further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65.

2. Feed assays calculated from the assays and weights of the products.

3. Diphenylguanidine.

4. Hematite produced in pilot plant studies at CSMRI; contains 280 ppm Ag.
Jarosite produced in laboratory by CANMET; silver-free.
Goethite obtained from Vieille Montagne; contains 130 ppm Ag.

recovery increased from 69.4% at pH 3 to 79% at pH 8 for hematite, 84.5 to 95.9% for ammonium jarosite, and 81.1 to 87.5% for goethite when using dispersant. It should be noted that the silver content of the hematite and goethite fraction of the mixtures was only 8% and 4% of the total silver input, respectively, indicating that the low silver recoveries were due to the slimes, and were not caused by the non-flotation of the silver in the slimes fraction. Although some of iron-bearing slimes were floated along with the silver, the high silver-containing concentrate and high concentration ratios as compared to the test without slimes, suggested that the flotation or entrainment of silica was prevented by the slimes. Diphenylguanidine and dispersant in the hematite system gave high silver recovery but the collected froth was difficult to handle.

Published data([5,7]) showed that naturally occurring cerargyrite in siliceous ores containing iron oxide slimes responded well in the standard sulphide flotation process. The low recovery obtained in the present investigation could be due to differences in the physiochemical nature of the slimes, since the slimes used are chemical precipitates obtained in the zinc hydrometallurgical process (except ammonium jarosite).

4.3.2 Silver Jarosite/Sand/Slimes Mixture

Tests with hematite and goethite slimes mixed with ground sand and silver jarosite were carried out and the results are given in Table XXIII. The floatability of silver jarosite in the presence of hematite or goethite slimes was significantly reduced, possibly due to slime coatings or electrostatic coagulation of oppositely charged particles. Mineralogical work on naturally occurring silver jarosite has been reported by Amoros and others([73]), and difficulties in the flotation recovery of silver jarosite associated with hematite and goethite have been reported.

TABLE XXIII

FLOTATION TESTS[1] WITH SILVER JAROSITE/SAND/SLIMES MIXTURES

Test No.	pH	Dispersant		Collectors		Assays ppm Ag			Ag Recovery in Conc. %	Slimes Phase[4]	Fe Recovery in Conc. %
		Name	g/T	Name	g/T	Feed[2]	Concentrate	Tails			
80	4.0	-	-	Oleic acid	400	2037	20,578	52	97.7	-	-
101	7.0	Na_2SiO_3	400	Oleic acid	400	699	1598	403	56.6	Hematite	-
102	3.0	Na_2SiO_3	400	Oleic acid	400	658	677	656	10.7	Hematite	-
106	4.0	Starch	560	Oleic acid	400	663	406	686	5.1	Hematite	-
159	9.5	Starch	560	Sulphonate	400	3207	6875	2700	26.1	Hematite	-
120	3.0	-	-	Oleic acid	400	618	546	623	5.7	Hematite	21.9
121	3.0	-	-	DPG[3]	480	688	586	695	4.9	Hematite	17.6
114	3.0	$(NaPO_4)_6$	400	Oleic acid	400	661	1860	550	24.0	Goethite	20.3
115	3.0	-	-	Oleic acid	400	629	1140	563	20.8	Goethite	27.0
117	8.0	$(NaPO_4)_6$	400	Oleic acid	400	617	1645	134	85.2	Goethite	56.8

1. 200 g of ground sand, 50 g of zinc leach residue slimes and silver mineral were slurried at 15% solids, and conditioned at the specified pH for 5 min. The pulp was then further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of Aerofroth 65.

2. Feed assays calculated from the assays and weights of the products.

3. Diphenylguanidine.

4. Hematite produced in pilot plant at CSMRI; contains 280 ppm Ag.
Goethite obtained from Vieille Montagne; contains 130 ppm Ag.

4.4 Conclusions

1. Flotation tests with ternary mixtures of silver minerals (cerargyrite and silver jarosite), ground sand and zinc plant slimes (hematite, goethite and ammonium jarosite) have indicated that the presence of oxidic iron slimes in zinc plant residues may well interfere with flotation of silver residue. The results with cerargyrite showed that the presence of slimes reduced silver recovery by 10-30%, depending on the type of slimes, dispersant used and pH. The adverse slimes effect was more pronounced for hematite and goethite than for ammonium jarosite, possibly due to the finer particle size of the former slimes.

2. Flotation of silver jarosite in the presence of hematite and goethite slimes using oleic acid or sulphonate collector gave very poor silver recovery at pH 3.0. No appreciable improvement in silver recovery was achieved by use of dispersants or floating at higher pH.

5. FLOTATION OF ZINC PLANT RESIDUES

The search of the literature on the flotation of silver and/or lead from zinc plant residues identified fourteen flotation processes (Table IV). Presently, Vieille Montagne (high acid leach residue), Dowa (acid reduction leach residue), Mitsubishi (sulphation roast-leach residue), and Zhuzhou (neutral leach residue) employ flotation processes for the recovery of silver and/or lead. At Espanola (neutral leach residue) flotation is utilized to recover the unroasted zinc.

Flotation tests using samples of pre-jarosite technology pond residue from CEZ, hematite residue produced from a proprietary process pilot plant operation, neutral leach residue produced in the CEZ pilot plant and high acid leach residue from Kidd Creek Mines Ltd. were carried out under conditions (i) indentified for flotation of silver minerals on the binary system with sand and (ii) published for the flotation of hydrometallurgical zinc plant residues.

The flotation processes evaluated in terms of silver flotation response were:

(i) Mitsubishi process:([42,43,44])

applied to sulphation roast-leach residue, pH 2-3, float silver with mercaptobenzothiazole (R-404)

(ii) Espanola process:([45])

applied to neutral leach residue, pH 5.0, float unroasted ZnS with xanthate after $CuSO_4$ activation

(iii) Zhuzhou process:([35])

applied to neutral residue, with or without superficial sulphidization, float silver with dithiophosphate

(iv) Outokumpu process:([53,54])

applicable to neutral leach residue, hematite residue and jarosite residue, pH 3-5, complete sulphidization (over 3 h) with silver and lead sulphides seeds, float silver and lead with conventional sulphide collectors

(v) MET-MEX Penoles process:([57])

applied to high acid leach residue, pH 2, float silver with unknown collector and then float lead with sulphonate

(vi) Asturiana process:([51])

applied to high acid leach residue, pH 2-4.5, straight silver flotation with conventional sulphide collectors and then superficial sulphidization for lead flotation, or combined silver-lead flotation after sulphidization

(vii) Vieille Montagne process:([52])

applied to high acid leach residue, pH 3, float silver with sulphide collectors and lead with sulphonate and acetate

(viii) Dowa process:([48,49,50])

applied to reduction leach residue or sulphation leach residue, pH 2-5, float silver with dithiophosphate then float lead with diamine

(ix) Toho process: ([59])

applied to neutral leach residue, pH 3, float lead (and silver) with combination of amine, sulphonate and dithiophosphate

(x) Binary conditions (present study)

natural pH (3-5), float silver with amyl xanthate or dithiophosphate with or without superficial sulphidization.

5.1 Sample preparation and Characterization

Four different zinc leach residues were used in the test work. A sample of moist pond residue was obtained from CEZ, dried at room temperature, and screened to minus 10 mesh.

The hematite residue was obtained from Noranda Research Centre as a wet filter cake, which was then dried at room temperature and screened to minus 10 mesh.

The high acid leach residue was obtained from Kidd Creek Mines as thick slurry. The moisture content was further reduced by filtration and the sample was used as a wet cake.

The neutral leach residue was prepared in the CEZ pilot plant according to the sequence shown in Figure 5. Calcine, produced by roasting of Brunswick zinc concentrate was leached for 1 hour with commercial spent electrolyte at 90°C to a residual acidity of ~15 g/L H_2SO_4. The slurry was then settled without flocculant addition and the solids were partially washed by decantation and filtration. The results of chemical and size analyses performed with the head samples are given in Tables XXIV and XXV, respectively.

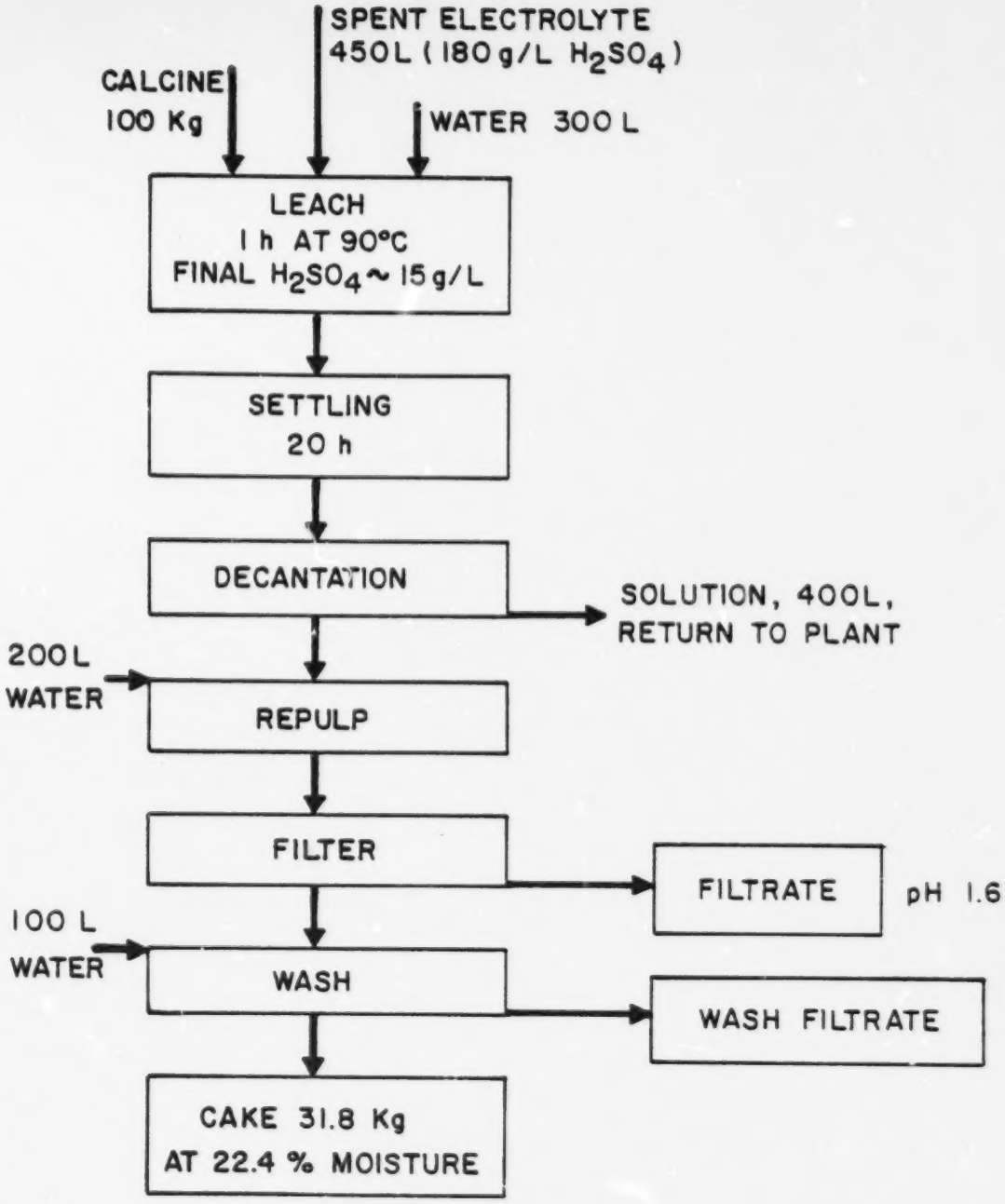

Figure 5 - Neutral Leach Residue Preparation in the CEZ Pilot Plant

TABLE XXIV

CHEMICAL ANALYSES OF ZINC LEACH RESIDUES

Sample	Assays, %					
	Ag	Pb	Zn	Fe	S_T	$S(SO_4)$
Pond residue	0.023	0.53	20.1	36.6	2.12	1.24
Hematite residue	0.019	0.84	4.67	43.8	4.01	3.77
HAL residue	0.149	6.84	4.06	19.4	10.4	4.55
N.L. residue	0.037	8.33	22.1	36.8	2.16	1.53

Mineralogical examination of the residues (Appendix IV) showed that the pond residue consisted of zinc ferrite, sphalerite, quartz and hematite, often cemented together by an amorphous iron hydroxide; no silver-bearing minerals were detected. The neutral leach residue consisted of fine-grained zinc ferrite, lead sulphate and sphalerite together with traces of hematite, magnetite and pyrite; silver was detected as an Ag_2S coating on one sphalerite grain. The HAL residue consisted of a jarosite-type compound, lead sulphate and sphalerite with minor amounts of hematite and zinc ferrite as well as traces of chalcopyrite, pyrite and gypsum; silver was closely associated with selenium, $Ag_2(S, Se)$, in masses of sulphur-silica gel and as thin coatings on sphalerite. There was also some evidence that the jarosite is silver-bearing.

XRD analysis of the hematite residue showed major phases of hematite, having poor crystallinity, and a jarosite-type compound, and a minor phase of zinc ferrite.

5.2 Experimental Procedure

In the initial part of the experimental work for the recovery of silver from the four zinc leach residues, a series of preliminary flotation tests was carried out under conditions identified for flotation of silver minerals in the binary system with sand. Experimentally, 250 g of residue was slurried at 15% solids and conditioned at pH 3 or pH 8 for 5 min. The pulp was then further conditioned for 5 min. with collector.

TABLE XXV

SIZE ANALYSES OF ZINC LEACH RESIDUES

Fraction, mesh	Wt. %	ASSAYS, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Sample 1: CEZ pond residue									
+200	4.4	0.024	0.46	15.2	-	4.9	3.8	3.3	-
200/270	5.2	0.0161	0.24	16.9	-	3.9	2.4	4.3	-
270/400	6.1	0.0126	0.20	17.0	-	3.6	2.3	5.1	-
400/500	7.5	0.0202	0.40	16.8	-	7.0	5.7	6.2	-
-500	76.8	0.0225	0.59	21.5	-	80.5	85.8	81.1	-
Total	100.0	0.0214	0.53	20.4	-	100.0	100.0	100.0	-
Sample 2: Hematite residue									
+200	4.2	0.0021	0.42	6.21	-	0.6	2.2	5.1	-
200/270	7.7	0.0021	0.30	7.21	-	1.2	2.8	10.9	-
270/400	7.6	0.0015	0.20	6.43	-	0.8	1.9	9.7	-
400/500	8.6	0.0016	0.28	6.39	-	1.0	3.0	10.8	-
-500	71.9	0.0187	1.01	4.48	-	96.4	90.1	63.5	-
Total	100.0	0.0140	0.81	5.07	-	100.0	100.0	100.0	-
Sample 3: High acid leach residue									
+500	5.3	0.13	1.58	7.04	19.3	4.7	1.2	9.3	5.3
-500	94.7	0.15	7.14	3.89	19.4	95.3	98.8	90.7	94.7
Total	100.0	0.15	6.84	4.06	19.4	100.0	100.0	100.0	100.0
Sample 4: Neutral leach residue									
+500	2.7	0.086	3.38	24.9	35.6	5.8	1.1	3.0	2.6
-500	97.3	0.039	8.36	22.0	37.6	94.2	98.9	97.0	97.4
Total	100.0	0.040	8.22	22.1	37.5	100.0	100.0	100.0	100.0

Roughing was conducted for 10 min. with the addition of frother (Aero-froth 65). In sulphidization tests, sulphidization was done at the given pH for the specific period before adding collector. Collectors and quantities used were 60 g/t amyl xanthate (R-350) and 10 g/t Aerofloat 25 (AF 25) for pond and hematite residues, and 60 g/t sodium diisoamyl dithiophosphate (R-3501) and 10 g/t Aerofloat 25 (AF 25) for neutral leach and high acid leach residues. Residue grinding to minus 400 mesh was also evaluated for pond residue.

In the second series of tests, silver flotation response was evaluated using the published flotation processes and the binary system flotation conditions with modifications such as (1) presence of flocculants, (2) flotation in the leach medium for neutral leach residue. The flotation response was determined by taking incremental froth samples during a 30-45 min. roughing period.

The next series of tests, using pond and neutral leach residues, was aimed at obtaining high grade silver concentrates by cleaning of the rougher concentrate. Experimentally, 1-kg batch tests were performed according to the processes given above and the rougher concentrates were cleaned in a 250 g cell. The roughing was done for 30 min. and cleanings were done for 7-10 min. Finally, a cycle test was carried out using neutral leach residue, in which the cleaner tails were recycled to the head of the next cycle.

Detailed conditions and laboratory data for each of the residue flotation tests are given in Appendix III.

5.3 Results and Discussion

5.3.1 C.E.Z. Pond Residue

5.3.1.1 Preliminary Tests

A series of preliminary flotation tests using pre-jarosite technology pond residue from CEZ was carried out to examine the silver flotation response with pH, regrinding and sulphidization. The results of 10-min. rougher flotation tests are shown in Table XXVI. It can be seen from the table that straight silver flotation using amyl xanthate

TABLE XXVI

ROUGHER FLOTATION OF CEZ POND RESIDUE

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/t	Sulphidization Time Min.	Assay, % Ag			Silver Recovery %	wt. % of conc.
				Feed[2]	Conc.	Tail		
161	3.0	-	-	0.025	0.162	0.013	50.4	7.7
163[3]	3.0	-	-	0.023	0.111	0.013	50.4	10.4
165	3.0	100	10	0.023	0.128	0.014	43.5	7.8
166[3]	3.0	100	10	0.025	0.107	0.015	47.4	11.2
162	8.0	-	-	0.023	0.146	0.015	42.4	6.8
168[3]	8.0	100	10	0.023	0.142	0.013	50.9	8.3

[1] 250 g of residue was slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with 60 g/t R-350 and 10 g/t AF 25. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

[2] Feed assays were calculated from the assays and weights of the products.

[3] Ground to minus 400 mesh.

[4] 1 kg/t sodium hexametaphosphate was added during repulping.

resulted in 10-min. rougher concentrate assaying 0.107-0.162% Ag with recoveries of 42.4-50.9%. The pulp pH, regrinding and superficial sulphidization prior to flotation did not affect the silver recovery. However, tests at pH 3.0 with regrinding or sulphidization floated more gangue material that lowered concentrate grade. The results above show that about 50% of the silver might be recovered using xanthate collector.

5.3.1.2 Flotation Rate Study

A second series of flotation tests was carried out using published silver flotation processes in order to examine the flotation responses of contained metals. Incremental froth samples up to 45-min. rougher flotation were taken. The results are given in Figures 6, 7 and 8 for the relationships between silver recovery and flotation time and cumulative silver grade. Data for metal distributions are given in Table XXVII.

The Mitsubishi process in which reagent 404 (Mercaptobenzothiazole) was used resulted in the 30-min. concentrate having 0.122% Ag with recovery of 63.4%. Other processes (Espanola, Zhuzhou and Binary) gave 49-58% silver recovery at grades of 0.102-0.149% Ag. The Toho process resulted in 60.3% silver recovery, but the concentrate contained only 0.07% Ag, indicating very poor selectivity. It is interesting to note that the use of R-404, which is generally used for the collection of oxidized sulphide ores, gave the highest silver grade and recovery.

Mineralogical examination (Appendix VI) of the 5-min. rougher concentrate produced using the Zhuzhou Process (Table XXVII, Test 196) showed that it consists of sphalerite and zinc ferrite together with minor amounts of hematite and traces of pyrite, quartz, chalcopyrite and silicates. Silver was present as rims of Ag_2S or $(Cu, Ag)_2S$ on sphalerite; inclusions of these sulphides in the larger sphalerite grains were also seen.

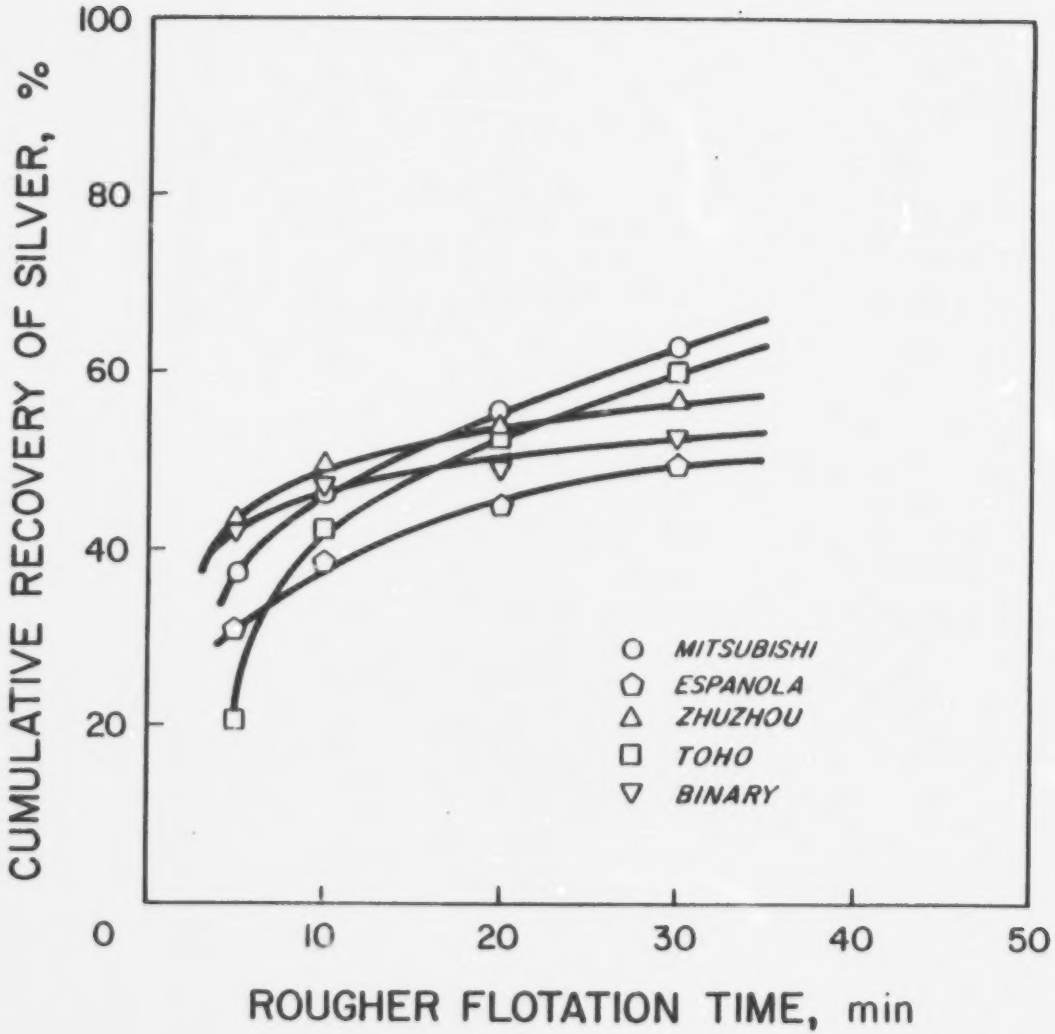

Figure 6 - Cumulative Silver Recovery Against Flotation Time (Pond Residue)

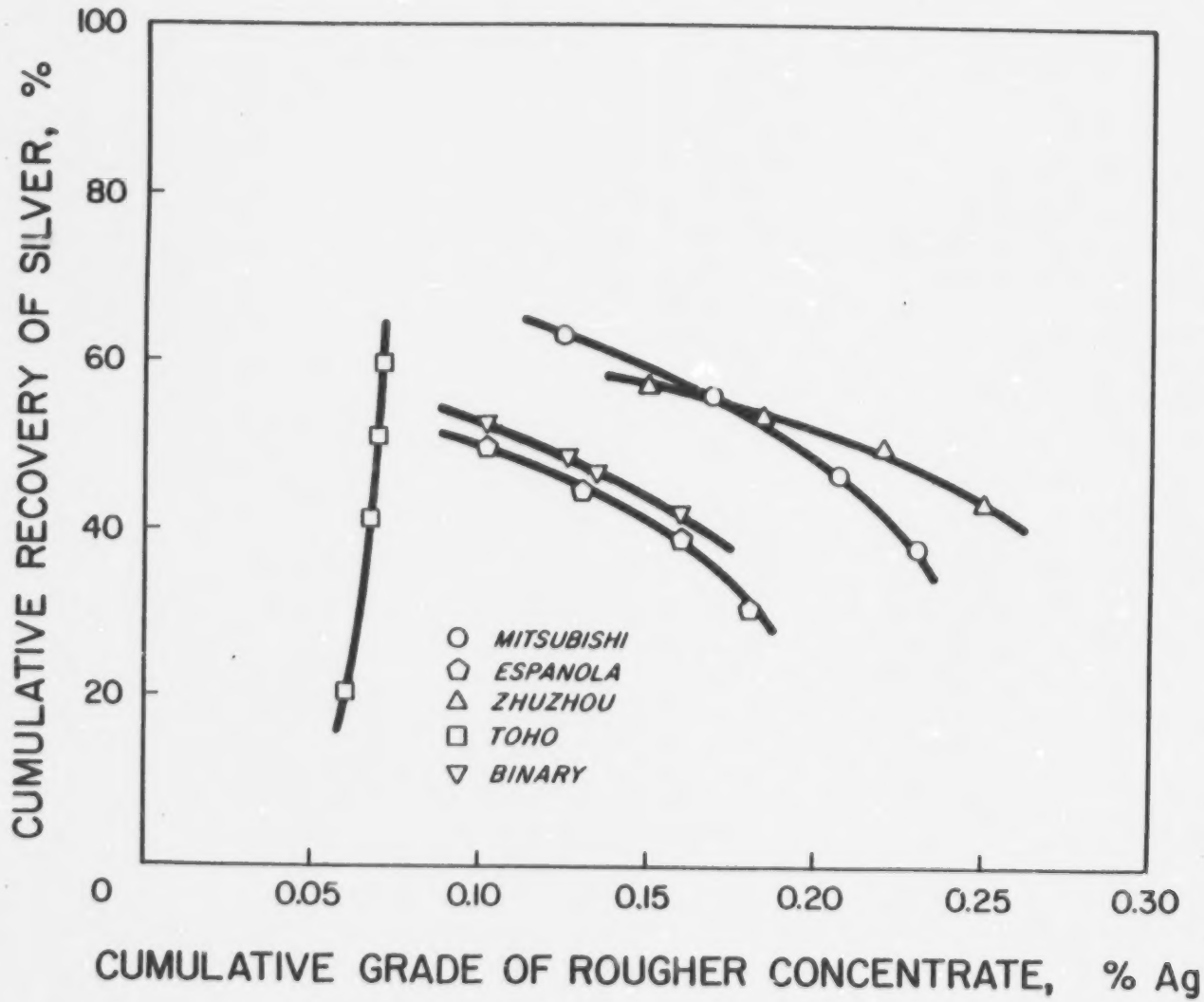

Figure 7 - Grade Recovery Relationship (Pond Residue)

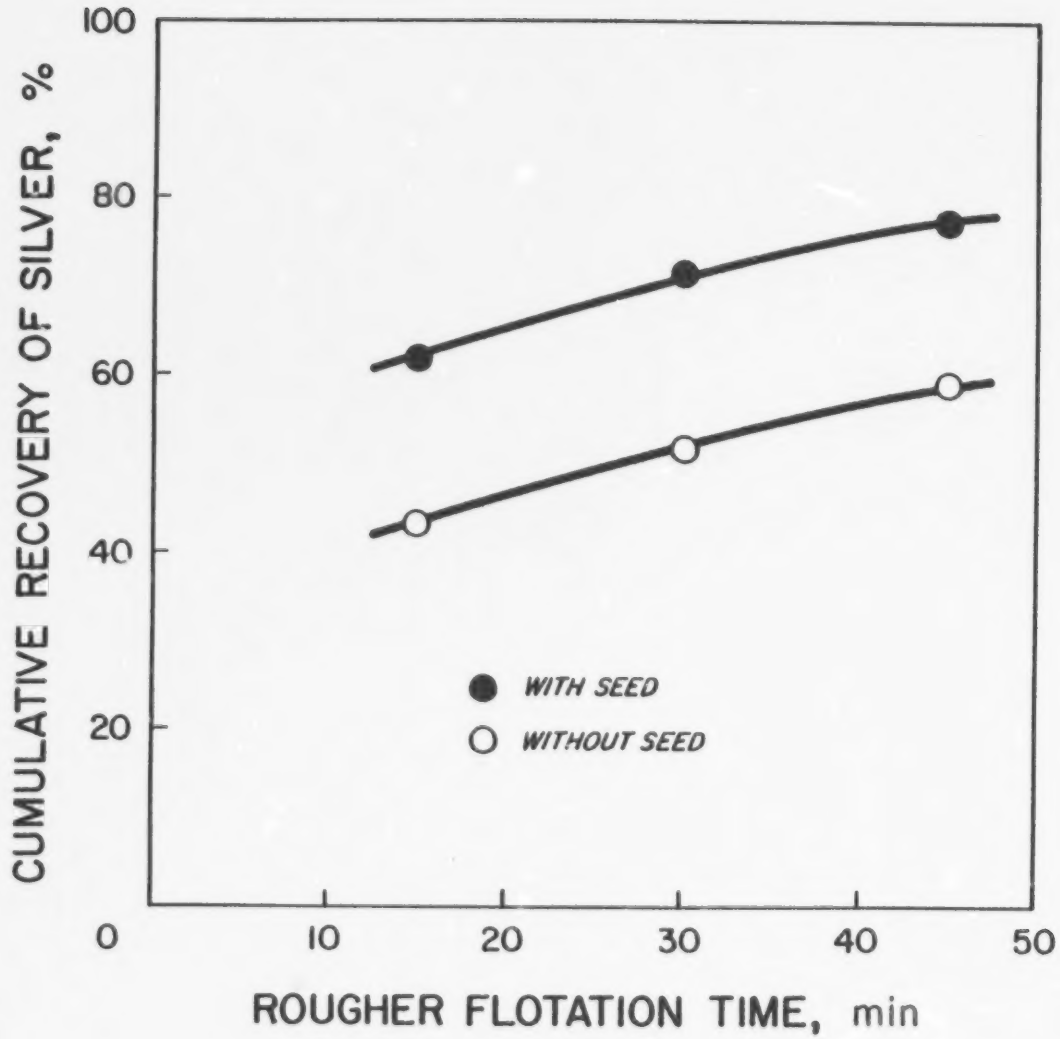

Figure 8 - Cumulative Silver Recovery Against Flotation Time with Pond Residue (Outokumpu Process)

TABLE XXVII

FLOTATION RATE TESTS WITH POND RESIDUE

Fraction	Wt. %	ASSAYS, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
T-194. Mitsubishi process. pH 3.0, R-404									
Conc 1	3.94	0.23	0.38	40.0	23.4	37.9	2.6	8.0	2.4
Conc 2	1.30	0.16	0.53	30.3	31.3	8.7	1.2	2.0	1.1
Conc 3	2.75	0.081	0.63	25.8	36.9	9.3	2.9	3.6	2.7
Conc 4	4.46	0.040	0.68	22.7	39.6	7.5	5.2	5.2	4.7
Tails	87.55	0.010	0.59	18.2	38.4	36.6	88.1	81.2	89.1
Heads	100.00	0.0239	0.58	19.6	37.7	100.0	100.0	100.0	100.0
T-195. Espanola process. pH 5.0, $CuSO_4.5H_2O$. R-350									
Conc 1	3.96	0.18	0.34	40.4	23.4	30.9	2.5	7.3	2.5
Conc 2	1.66	0.11	0.57	28.2	34.1	7.9	1.7	2.1	1.5
Conc 3	2.29	0.064	0.62	25.2	36.9	6.3	2.6	2.6	2.3
Conc 4	2.74	0.037	0.65	23.6	38.4	4.5	3.4	3.0	2.8
Tails	89.35	0.013	0.54	20.8	38.0	50.4	89.8	85.0	90.9
Heads	100.0	0.0230	0.54	21.9	37.3	100.0	100.0	100.0	100.0
T-196. Zhuzhou process. pH 3.0, $Na_2S.9H_2O$. R-3501									
Conc 1	4.09	0.25	0.30	43.1	20.8	43.5	2.3	8.9	2.3
Conc 2	1.24	0.12	0.60	26.6	35.7	6.4	1.4	1.6	1.2
Conc 3	1.51	0.061	0.81	24.4	38.8	3.9	2.3	1.8	1.5
Conc 4	2.19	0.038	0.68	23.3	39.3	3.6	2.7	2.6	2.3
Tails	90.97	0.011	0.54	18.6	38.2	42.6	91.3	85.1	92.7
Heads	100.00	0.0235	0.54	19.9	37.5	100.0	100.0	100.0	100.0
T-219. Binary process. pH 3.0, R-350, R-25									
Conc 1	5.85	0.16	0.49	38.6	-	42.1	5.6	10.2	-
Conc 2	1.81	0.06	0.65	26.6	-	4.9	2.4	2.2	-
Conc 3	0.95	0.044	0.65	26.9	-	1.9	1.2	1.2	-
Conc 4	2.80	0.027	0.62	26.4	-	3.4	3.4	3.3	-
Tails	88.59	0.012	0.50	20.8	-	47.8	87.4	83.1	-
Heads	100.0	0.0222	0.51	22.2	-	100.0	100.0	100.0	-
T-197. Outokumpu process. pH 3.0, 3-m sulphidization, 40°C without seed.									
Conc 1	6.93	0.155	0.42	35.7	27.6	43.3	5.3	11.8	4.9
Conc 2	3.47	0.062	0.67	22.6	39.2	8.7	4.2	3.7	3.5
Conc 3	4.47	0.038	0.68	22.5	39.7	6.8	5.4	4.9	4.6
Tails	85.13	0.012	0.55	19.6	39.6	41.2	85.1	79.6	87.0
Heads	100.0	0.0248	0.56	20.9	38.7	100.0	100.0	100.0	100.0
T-206. Outokumpu process with seed.									
Conc 1	6.83	0.36	5.22	36.8	21.9	61.9	39.8	11.5	4.1
Conc 2	6.50	0.059	0.79	24.4	37.2	9.7	5.7	7.2	6.6
Conc 3	5.02	0.046	0.79	24.6	37.0	5.8	4.4	5.7	5.1
Tails	81.65	0.011	0.55	20.2	37.6	22.6	50.1	75.6	84.2
Heads	100.0	0.0397	0.90	21.8	36.5	100.0	100.0	100.0	100.0
T-204. Toho process. pH 3.0, Amine, R-3501, R-899									
Conc 1	9.23	0.0609	1.08	24.6	35.1	21.2	18.2	10.8	8.6
Conc 2	6.50	0.0861	0.77	28.9	31.1	21.2	9.1	8.9	5.4
Conc 3	4.07	0.0720	0.71	25.8	35.0	11.1	5.3	5.0	3.8
Conc 4	2.97	0.0606	0.76	23.7	37.1	6.8	4.1	3.4	2.9
Tails	77.22	0.0136	0.45	19.6	38.5	39.7	63.3	71.9	79.3
Heads	100.0	0.0264	0.55	21.0	37.5	100.0	100.0	100.0	100.0

The flotation results using the Outokumpu process, which involves 3-h of sulphidization with 100% stoichiometric ratio of sulphide (7.2 kg/T $Na_2S \cdot 9H_2O$) to silver and lead with and without seed (argentite and galena), show that a silver recovery of 58.8% was obtained after 45-min. roughing without seed. Tests with seed gave 77.4% overall silver recovery (including seed silver) but corrected recoveries show that the effect of seed on silver or lead recoveries from the residue feed was almost negligible.

5.3.1.3 Cleaning Tests

A series of tests was carried out to obtain a high-grade silver concentrate using four of the promising processes evaluated above. In each test, 1-kg residue was slurried at 30% solids and conditioned according to the selected process conditions. A 30-min. rougher concentrate was produced and cleaned two times at the same pH in a 250 g cell with the addition of small amounts of reagent. The cleaner flotation time was 10 min. for the first cleaning and 5-8 min. for the second cleaning.

The results (Table XXVIII) show that the Binary process, with R-350 and AF 25 collectors at pH 3.0, gave a twice-cleaned concentrate assaying 0.37% Ag, 62.5% Zn and 5.93% Fe with recoveries of 41.2% silver, 7.6% zinc and 0.4% iron. The rougher tail assayed 0.012% Ag, 19.7% Zn and 36.8% Fe, and contained 46.5% of the silver and 83.4% of the zinc in the feed.

The Mitsubishi process with collector R-404 produced a concentrate assaying 0.39% Ag and 59.2% Zn with recoveries of 46.3% silver and 7.7% zinc. The Espanola process gave a cleaner concentrate assaying 0.29% Ag and 60.1% Zn with recoveries of 32.0% silver and 6.9% zinc. The Zhuzhou process, in which superficial sulphidization was used prior to flotation, resulted in a concentrate assaying 0.31% Ag and 58.6% Zn with recoveries of 41.8% silver and 7.9% zinc.

TABLE XXVIII

CLEANER FLOTATION TESTS WITH POND RESIDUE

Fraction	Wt. %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
T-227. Binary process.									
Conc	2.59	0.37	0.06	62.5	5.93	41.2	0.3	7.6	0.4
Cl 2 Tail	0.80	0.083	0.61	25.1	38.1	2.9	0.9	0.9	0.8
Cl 1 Tail	6.64	0.033	0.62	25.9	37.7	9.4	7.8	8.1	7.0
R-Tail	89.97	0.012	0.53	19.7	36.8	46.5	91.0	83.4	91.8
Heads	100.00	0.0232	0.52	21.3	36.1	100.0	100.0	100.0	100.0
T-228. Mitsubishi process.									
Conc	2.70	0.39	0.06	59.2	7.0	46.3	0.3	7.7	0.5
Cl 2 Tail	0.58	0.107	0.62	25.4	37.4	2.8	0.6	0.7	0.6
Cl 1 Tail	4.43	0.032	0.59	26.4	35.4	6.2	4.8	5.6	4.4
R-Tail	92.29	0.011	0.56	19.4	36.8	44.7	94.3	86.0	94.5
Heads	100.00	0.0227	0.55	20.8	35.9	100.0	100.0	100.0	100.0
T-229. Espanola process.									
Conc	2.41	0.29	0.06	60.1	6.81	32.0	0.3	6.9	0.5
Cl 2 Tail	0.65	0.17	0.63	25.6	35.8	5.0	0.7	0.8	0.6
Cl 1 Tail	5.89	0.033	0.58	29.7	31.9	8.9	6.2	8.3	5.2
R-Tail	91.05	0.013	0.56	19.4	36.9	54.1	92.8	84.0	93.7
Heads	100.00	0.0219	0.55	21.0	35.9	100.0	100.0	100.0	100.0
T-230. Zhuzhou process.									
Conc	2.85	0.31	0.08	58.6	8.87	41.8	0.5	7.9	0.7
Cl 2 Tail	2.10	0.04	0.62	24.8	37.0	4.0	3.1	2.5	2.2
Cl 1 Tail	10.06	0.021	0.63	24.7	37.1	10.0	14.8	11.8	10.6
R-Tail	84.99	0.011	0.41	19.3	35.8	44.2	81.6	77.8	86.5
Heads	100.00	0.0211	0.43	21.1	35.2	100.0	100.0	100.0	100.0

The results show that (i) due to the oxidized character of the residue, the mercaptan-type collector (R-404) gave the highest silver recovery and (ii) the residue seems to contain readily floatable silver, activable silver and unfloatable silver. Therefore, a set of tests employing two-stage flotation (10 min. per stage) was carried out with first stage collector as the variable. The floatable silver was first floated with xanthate or R-404 followed by sulphidization and flotation with collector R-3501.

The results are given in Table XXIX. The xanthate float gave 51% overall silver recovery, while the R-404 float resulted in 62.7% silver recovery. The tails assayed 0.012% Ag in the xanthate float and 0.0089% Ag in the R-404 float. More work is needed in this direction.

5.3.2 Neutral Leach Residue

5.3.2.1 Preliminary Tests

The flotation response of silver with the neutral leach residue was evaluated in a series of tests using dithiophosphates as collectors at pH 3 and pH 8, with and without superficial sulphidization. The results are given in Table XXX. At pH 3.0, silver recovery of 54.9% at a grade of 0.318% Ag was obtained without sulphidization. Sulphidization tests with 100-300 g/T $Na_2S \cdot 9H_2O$ for 10-30 min. resulted in concentrates assaying 0.275% Ag with recoveries of 64-66% silver. The tails assayed 0.014% Ag. At pH 8.0 sulphidization seemed to increase the silver recovery, however, simultaneous flotation of other constituents lowered the concentrate grade. The preliminary results indicate that the residue contains readily floatable silver as well as some silver that requires superficial sulphidization, by which about 10% additional silver recovery can be achieved.

5.3.2.2 Flotation Rate Study

A series of flotation tests using the published silver flotation processes was carried out to investigate the flotation response by

TABLE XXIX

TWO-STAGE ROUGHER FLOTATION OF POND RESIDUE

FRACTION	WT %	ASSAYS, %			DISTRIBUTION, %		
		Ag	Pb	Zn	Ag	Pb	Zn
T- 220. Xanthate float then sulphidization-float.							
conc. 1	6.53	0.15	0.25	41.7	44.5	3.4	12.0
conc. 2	3.73	0.038	0.46	26.4	6.5	3.6	4.3
R-tail	89.74	0.012	0.49	21.2	49.0	93.0	83.7
Heads	100.0	0.0220	0.47	22.7	100.0	100.0	100.0
T-221. R-404 float then sulphidization-float.							
conc. 1	7.26	0.15	0.43	41.8	52.5	6.6	13.1
conc. 2	5.74	0.037	0.60	27.5	10.2	7.2	6.8
R-tail	87.00	0.0089	0.47	21.3	37.3	86.2	80.1
Heads	100.00	0.0208	0.47	23.1	100.0	100.0	100.0

TABLE XXX

ROUGHER FLOTATION OF NEUTRAL LEACH RESIDUE

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/t	Sulphidization Time min.	Assay, % Ag			Silver Recovery %	wt. % of conc.
				Feed[2]	Conc.	Tail		
Neutral Leach Residue (0.037% Ag, 8.33% Pb)								
181	3.0	-	-	0.037	0.318	0.018	54.9	6.4
183	3.0	100	10	0.036	0.276	0.014	63.9	8.3
185	3.0	300	30	0.038	0.275	0.014	66.1	9.0
182	8.0	-	-	0.036	0.107	0.023	46.8	15.9
184	8.0	100	10	0.037	0.112	0.017	64.2	21.3

[1] 250 g of residue was slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with 60 g/t R-3501 and 10 g/t AF 25. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

[2] Feed assays were calculated from the assays and weights of the products.

analyzing timed froth samples. The results are given in Table XXXI and the silver recoveries, as a function of flotation time and concentrate grade, are shown in Figures 9, 10 and 11.

The Mitsubishi process resulted in a silver recovery of 68% after 30 min. flotation giving 0.239% Ag in the concentrate. The tails assayed 0.013% Ag. The Espanola, Zhuzhou and Binary processes, however, gave 77.7-81.6% silver recovery with concentrate assaying 0.197-0.326% Ag and tails assaying only 0.008% Ag.

The Outokumpu process, with and without seed, gave the highest silver recoveries (85-90%), however, the prolonged sulphidization required with high dosage of $Na_2S \cdot 9H_2O$ (20-100 kg/T) at elevated temperature reduces the attractiveness of this approach. The Toho process resulted in an overall silver recovery of 76.8%, but the silver content in the concentrate was again extremely low because of non-selectivity. However, the process did float lead, giving an overall lead recovery in 30 min. roughing of 88.2%.

It is quite obvious from the results that the freshly prepared neutral leach residue behaves much differently than the pond residue, which gave about 50% silver recovery with similar flotation processes. The flotation rate study results suggest that the production of high-grade silver concentrate (over 1% Ag) with about 70% recovery may be possible if the rougher concentrate is cleaned.

Mineralogical examination (Appendix IV) of the 5 min. rougher concentrate produced using the Zhuzhou Process (Table XXXI, Test 192) showed that it consists of sphalerite and zinc ferrite together with a trace of quartz. Most of the sphalerite grains were rimmed by a continuous layer of Pb-Ag sulphide.

5.3.2.3 Cleaning and Locked Cycle Tests

A series of batch cleaning tests and a locked cycle test were carried out to study the possibility of producing high-grade silver

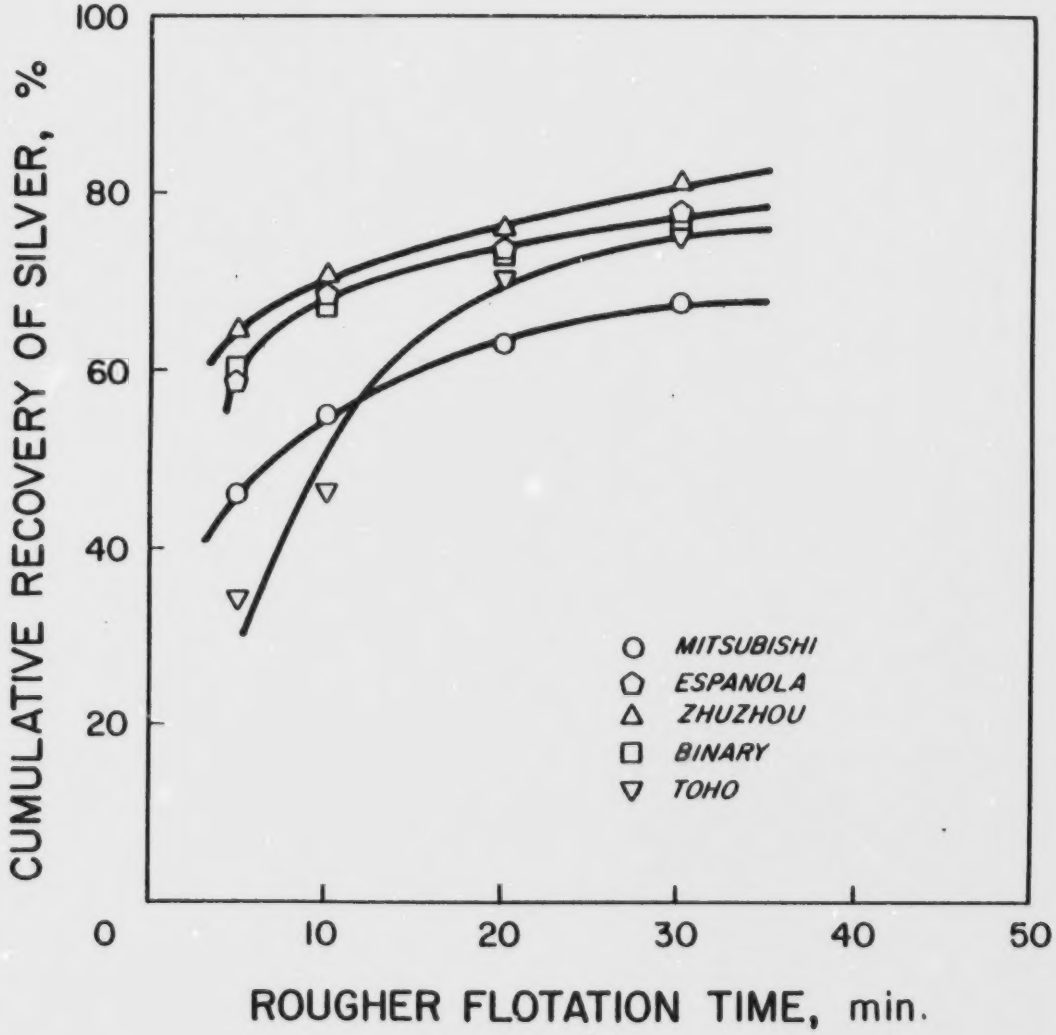

Figure 9 - Cumulative Silver Recovery Against Flotation Time
(Neutral Leach Residue)

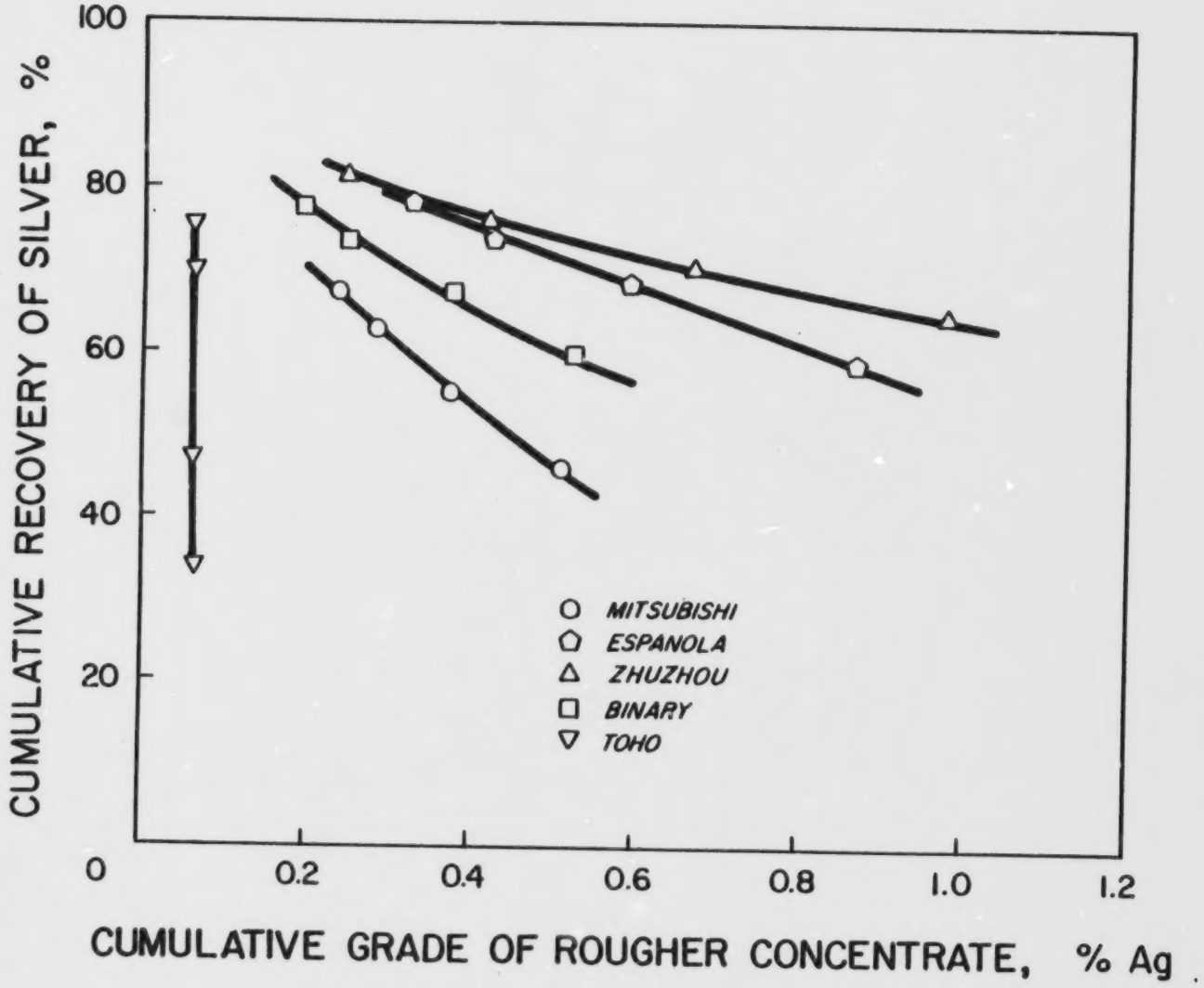

Figure 10 - Grade Recovery Relationship (Neutral Leach Residue)

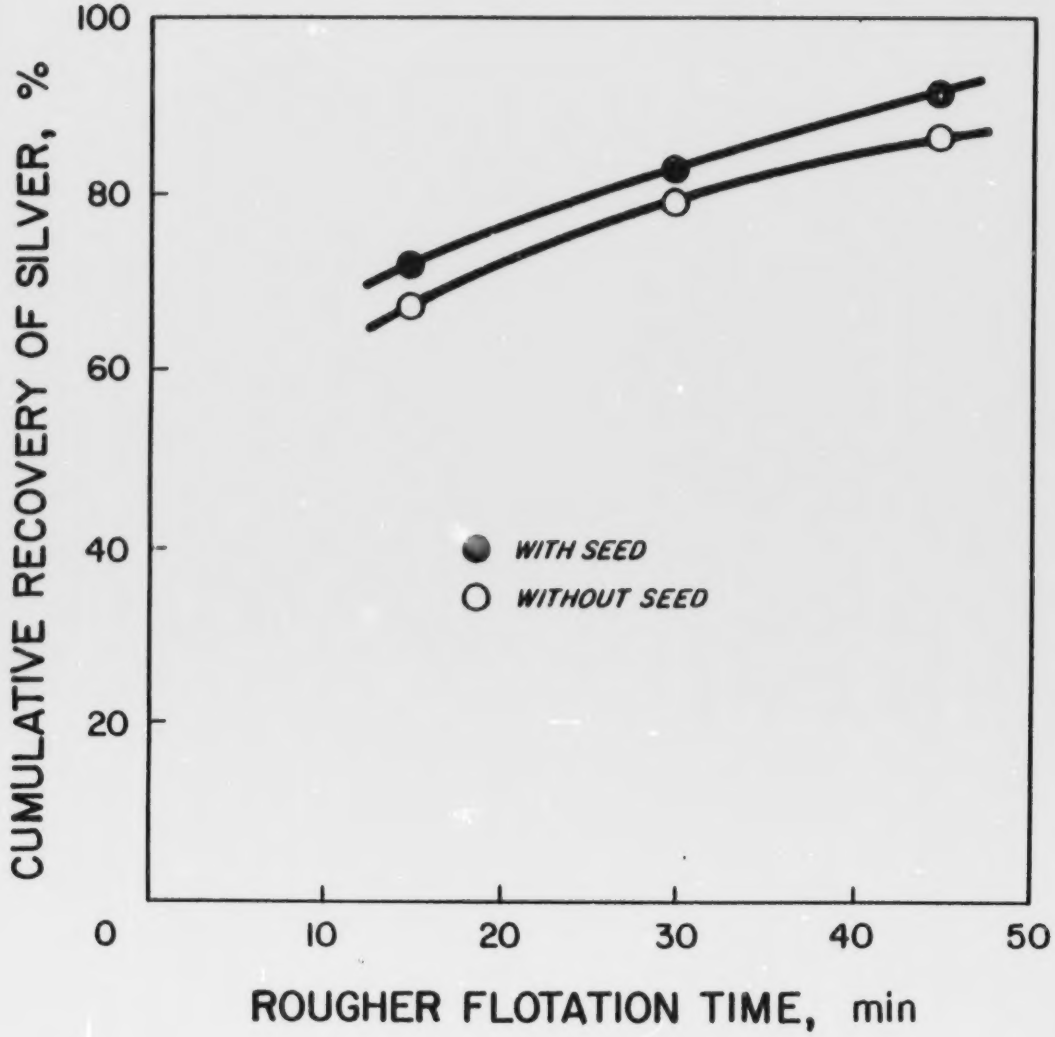

Figure 11 - Cumulative Silver Recovery Against Flotation Time
(Outokumpu Process)

TABLE XXXI

FLOTATION RAT: TESTS WITH NEUTRAL LEACH RESIDUE

Fraction	Wt. %	ASSAYS, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
T-190. Mitsubishi process. pH 3.0, R-404									
Conc 1	3.30	0.51	5.76	30.8	29.7	46.2	2.4	4.4	2.7
Conc 2	2.02	0.16	6.19	26.6	33.4	8.9	1.6	2.3	1.8
Conc 3	2.69	0.11	7.27	25.9	35.1	8.1	2.5	3.0	2.6
Conc 4	2.36	0.075	7.40	25.4	35.1	4.8	2.2	2.5	2.3
Tails	89.63	0.013	8.04	22.8	36.8	32.0	91.3	87.8	90.6
Heads	100.00	0.0364	7.89	23.3	36.4	100.0	100.0	100.0	100.0
T-191. Espanola process. pH 5.0, $CuSO_4.5H_2O$, R-350									
Conc 1	2.51	0.87	4.46	35.1	23.0	59.3	1.4	3.8	1.6
Conc 2	1.78	0.20	6.14	27.3	32.2	9.7	1.4	2.2	1.6
Conc 3	2.14	0.089	7.10	26.5	33.1	5.2	1.9	2.5	2.0
Conc 4	2.38	0.061	7.40	26.1	34.3	4.0	2.2	2.7	2.3
Tails	91.19	0.0088	8.16	22.3	36.3	21.8	93.1	88.8	92.5
Heads	100.00	0.0367	7.99	22.9	35.8	100.0	100.0	100.0	100.0
T-192. Zhuzhou process. pH 3.0, Sulphidization, R-3501									
Conc 1	2.40	0.98	3.96	35.7	22.0	65.0	1.2	3.8	1.5
Conc 2	1.43	0.15	7.00	26.8	32.9	5.9	1.3	1.7	1.3
Conc 3	2.71	0.069	6.22	25.9	33.7	5.2	2.1	3.2	2.5
Conc 4	5.49	0.036	7.43	24.9	34.7	5.5	5.2	6.1	5.3
Tails	87.97	0.0076	8.05	21.6	36.6	18.4	90.2	85.2	89.4
Heads	100.00	0.0362	7.85	22.3	36.0	100.0	100.0	100.0	100.0
T-222. Binary process. pH 3.0, Sulphidization, R-350									
Conc 1	3.59	0.52	5.37	34.2	-	60.0	2.4	4.6	-
Conc 2	1.91	0.11	7.14	27.9	-	6.7	1.7	2.0	-
Conc 3	3.86	0.058	7.73	27.4	-	7.2	3.8	4.0	-
Conc 4	2.90	0.041	7.54	30.1	-	3.8	2.7	3.3	-
Tails	87.74	0.0079	8.02	26.1	-	22.3	89.4	86.1	-
Heads	100.00	0.0311	7.88	26.6	-	100.0	100.0	100.0	-
T-193. Outokumpu process. pH 3.0, 3-h sulphidization, R-3501 without seed									
Conc 1	5.81	0.43	25.6	20.6	19.9	67.2	17.6	5.3	3.2
Conc 2	2.72	0.16	19.6	21.1	26.8	11.7	6.3	2.5	2.0
Conc 3	4.15	0.069	15.6	21.5	30.2	7.7	7.7	3.9	3.4
Tails	87.32	0.0057	6.62	23.1	38.0	13.4	68.4	88.3	91.4
Heads	100.00	0.0372	8.45	22.8	36.3	100.0	100.0	100.0	100.0
T-207. Outokumpu process. with seed									
Conc 1	21.69	0.25	30.0	17.0	20.2	72.6	47.5	16.1	13.2
Conc 2	10.50	0.075	18.8	22.1	28.8	10.5	14.4	10.2	9.1
Conc 3	10.48	0.055	13.3	23.6	31.8	7.7	10.2	10.8	10.1
Tails	57.33	0.012	6.68	25.1	39.0	9.2	27.9	62.9	67.6
Heads	100.00	0.0747	13.70	22.9	33.1	100.0	100.0	100.0	100.0
T-203. Toho process. pH 3.5, Amine, sulphonate, R-3501									
Conc 1	20.00	0.064	24.9	16.8	25.5	34.7	60.1	14.2	14.0
Conc 2	6.51	0.070	14.6	20.7	31.5	12.4	11.5	5.7	5.6
Conc 3	15.02	0.059	8.12	24.1	36.9	23.8	14.7	15.3	15.3
Conc 4	2.33	0.093	6.70	24.3	36.8	5.9	1.9	2.4	2.4
Tails	56.14	0.015	1.75	26.3	40.5	23.2	11.8	62.4	62.7
Heads	100.00	0.0370	8.29	23.6	36.3	100.0	100.0	100.0	100.0

concentrate. A 1-kg residue sample was used in the batch cleaning tests and each batch of the cycle test. The three most promising processes were tested for batch cleaning and the Zhuzhou process was selected for the cycle test, in which the two cleaner tails pulps were recycled to the next stage roughing without filtration.

The results of batch cleaning tests are given in Table XXXII. The Mitsubishi process, in which R-404 (Mercaptobenzothiazole) is used as collector, resulted in a twice cleaned concentrate assaying 1.75% Ag, 45.8% Zn and 11.3% Fe with recoveries of 63.3% silver, 2.2% zinc and 0.4% iron. The rougher tails assayed 0.0088% Ag, 8.42% Pb, 22.6% Zn and 34.7% Fe, and contained 24.1% of the silver, 92.6% of the lead, 84.9% of the zinc and 90.9% of the iron in the feed. The Espanola process, which involves copper activation and xanthate flotation at pH 5, gave a cleaner concentrate assaying 1.93% Ag, 45.6% Zn and 9.16% Fe with recoveries of 70.8% silver, 2.5% zinc and 0.3% iron. The tails assayed 0.0064% Ag, 22.2% Zn and 34.7% Fe, and contained 17.0% of the silver, 87.9% of the zinc and 92.7% of the iron in the feed. Very similar results were obtained with the Zhuzhou process.

The above results show that it is possible to produce a high grade silver concentrate (>1.5% Ag) with over 80% silver recovery in the roughing stage. However, the Mitsubishi process recovered less silver than the other processes possibly because the collector used (R-404) was not as effective for fresh leach residue as it was for the oxidized pond residue.

The results of the locked cycle test are given in Table XXXIII and the calculated silver balance is given in Table XXXIV. The results show that a twice-cleaned silver concentrate assaying (average) 1.5% Ag, 1.5% Pb, 36.4% Zn and 12.0% Fe can be produced with a silver recovery of 77% from a feed assaying 0.032% Ag. It should also be noted that the rougher tails assayed only 0.0062-0087% Ag and the recoveries of zinc, lead and iron in the silver concentrate were 3.4%, 0.3% and 0.7%, respectively. The circulating load of the cleaner tails was about 17.4% of the feed weight.

TABLE XXXII

CLEANER FLOTATION TESTS WITH NEUTRAL LEACH RESIDUE

Fraction	Wt, %	ASSAYS, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
T-231. Mitsubishi process. pH 3.0, R-404									
Conc	1.12	1.75	1.07	45.8	11.3	63.3	0.1	2.2	0.3
Cl 2 Tail	1.22	0.098	7.28	29.5	32.0	3.8	1.1	1.5	1.2
Cl 1 Tail	8.56	0.032	5.87	32.1	29.9	8.8	6.2	11.5	7.5
R-Tail	89.10	0.0084	8.42	22.6	34.7	24.1	92.6	84.8	90.9
Heads	100.0	0.0311	8.11	23.8	34.0	100.0	100.0	100.0	100.0
T-232. Espanola process. pH 5.0, $CuSO_4$ activation, R-350									
Conc	1.26	1.93	0.83	45.6	9.16	70.8	0.1	2.5	0.3
Cl 2 Tail	0.91	0.17	4.97	32.8	28.2	4.5	0.6	1.3	0.7
Cl 1 Tail	6.64	0.04	7.15	28.9	32.3	7.7	6.2	8.3	6.3
R-Tail	91.19	0.0064	7.84	22.2	34.7	17.0	93.1	87.8	92.7
Heads	100.00	0.0344	7.68	23.0	34.2	100.0	100.0	100.0	100.0
T-233. Zhuzhou process. pH 3.0, 100 g/T $Na_2S.9H_2O$, R-3501									
Conc	1.28	1.66	0.85	48.0	8.89	67.4	0.1	2.5	0.3
Cl 2 Tail	1.02	0.152	6.27	30.5	30.2	4.9	0.8	1.3	0.9
Cl 1 Tail	9.66	0.033	7.36	28.0	32.8	10.0	8.6	11.0	9.3
R-Tail	88.04	0.0064	8.53	23.6	34.6	17.7	90.5	85.2	89.5
Heads	100.00	0.0317	8.30	24.5	34.1	100.0	100.0	100.0	100.0

TABLE XXXIII

LOCKED CYCLE FLOTATION TEST [1.] WITH NEUTRAL LEACH RESIDUE

Product		Assays, %			
		Ag	Pb	Zn	Fe
Concentrate Cycle	1	1.454	1.22	38.6	10.5
	2	1.379	2.05	34.9	13.9
	3	1.072	2.34	32.2	16.5
	4	1.603	1.42	36.3	11.7
	5	1.764	0.98	38.0	9.94
	6	1.779	0.76	39.5	9.14
	7	1.710	0.64	38.7	8.81
Weighted Average		1.495	1.46	36.43	12.0
Heads		0.0328	7.51	21.2	34.7
Tails Cycle	1	0.0072	7.58	20.2	35.1
	2	0.0073	7.21	20.4	35.4
	3	0.0062	7.38	20.8	35.0
	4	0.0087	7.39	20.9	35.8
	5	0.0087	7.73	21.4	35.1
	6	0.0073	8.07	21.6	35.1
	7	0.0075	7.98	20.6	35.0
Weighted Average		0.0076	7.62	20.87	35.2

[1.] Rougher flotation was conducted in a 1 kg flotation cell at 25% solids and natural pH (4.0-4.1). Rougher pulp was sulphidized with 100 g/T $Na_2S.9H_2O$ for 10 min and then conditioned with 100 g/T collector (R-3501) for a further 10 min. Rougher flotation was conducted for 30 min, with the addition of another 50 g/T collector during roughing, using AF-65 as frother.

Cleaning was conducted in a 250 g flotation cell at pH 4.0 and 25% solids using 10 g/T collector (R-3501) and AF-65 frother. Flotation time during cleaning was 10 min in the first stage, and 8 min in the second stage.

TABLE XXXIV

SILVER BALANCE IN LOCKED CYCLE FLOTATION

Charge			Clean Conc.		Rougher Tails		Cleaner Tails (Calculated)		Ag Recovery %
Cycle	Wt g	% Ag	Wt g	% Ag	Wt g	% Ag	Wt g	% Ag	
1	977.9	0.0328	13.0	1.454	816.7	0.0072	148.2	0.0492	78.4
2	976.2	0.0345	15.9	1.379	915.9	0.0073	192.6	0.0639	79.2
3	975.3	0.0313	22.0	1.072	950.1	0.0062	195.8	0.0677	80.6
4	976.1	0.0319	14.3	1.603	980.5	0.0087	177.1	0.0725	73.1
5	976.3	0.0315	13.6	1.764	976.9	0.0087	162.9	0.0675	72.7
6	976.9	0.0335	12.9	1.779	972.5	0.0073	154.4	0.0881	78.5
7	977.6	0.0319	13.3	1.710	962.5	0.0075	156.2	0.0944	76.8

5.3.2.4 Effect of Flotation Medium

A set of flotation tests using diluted zinc electrolyte was carried out to evaluate the effect of dissolved salts in the system, and hence the degree of residue washing required prior to flotation. (All prior neutral leach residue flotation tests have been performed by repulping the partially washed neutral leach residue filter cake with water to 25% solids, which results in a flotation medium having a natural pH of 3.8-4.1 and assaying 2.3 g/L Zn, 0.006 g/L Cu, 0.005 g/L Cd and 0.014 g/L Fe.) The tests were conducted by slurrying the neutral leach residue at 25% solids with diluted zinc leach solution (pH 1.6, 63.3 g/L Zn, 0.19 g/L Cu, 0.074 g/L Cd, 1.10 g/L Fe) and then floating at natural pH (1.7) according to the Espanola and Mitsubishi processes. Rougher flotation only was conducted for 30 min., with froth samples taken at 5, 10, 20 and 30 min.

The results of flotation tests are given in Table XXXV and silver recovery as a function of flotation time is shown in Figure 12. As can be seen, the silver recovery was reduced about 25% for the Espanola process when silver was floated in leach liquor as compared to water. On the other hand, the Mitsubishi process gave virtually no flotation. The poor flotation response may be due to the low pulp pH and/or high ionic strength of the medium in which the collecting power of the reagents is reduced by decomposition or through the formation of metal-collector complexes.

These results indicate the need for some washing of the leach residue prior to flotation, but more work is required to define the effects of ionic strength, pH, etc., on the flotation before the residue wash requirements can be specified.

TABLE XXXV

RESULTS OF FLOTATION TESTS USING LEACH SOLUTION AS FLOTATION MEDIUM

FRACTION	WT %	ASSAYS, %			DISTRIBUTION, %		
		Ag	Pb	Zn	Ag	Pb	Zn
T-223. Espanola process, pH 1.6							
conc. 1	3.16	0.25	6.00	31.7	25.6	2.8	3.8
conc. 2	2.34	0.11	6.89	28.4	8.4	2.5	2.6
conc. 3	3.93	0.099	7.68	27.7	12.6	4.5	4.1
conc. 4	3.40	0.074	7.17	28.1	8.2	3.6	3.7
Tail	87.17	0.016	6.65	25.7	45.2	86.6	85.8
Heads	100.00	0.0308	6.69	26.1	100.0	100.0	100.0
T-224. Mitsubishi process, pH 1.7							
conc. 1	2.49	0.024	7.31	27.7	2.0	2.5	2.7
conc. 2	1.72	0.024	7.12	27.3	1.3	1.7	1.8
conc. 3	3.98	0.033	7.37	27.7	4.3	4.1	4.3
conc. 4	2.75	0.089	7.49	28.8	8.1	2.8	3.0
Tail	89.06	0.028	7.20	25.5	84.3	88.9	88.2
Heads	100.00	0.0303	7.22	25.8	100.0	100.0	100.0

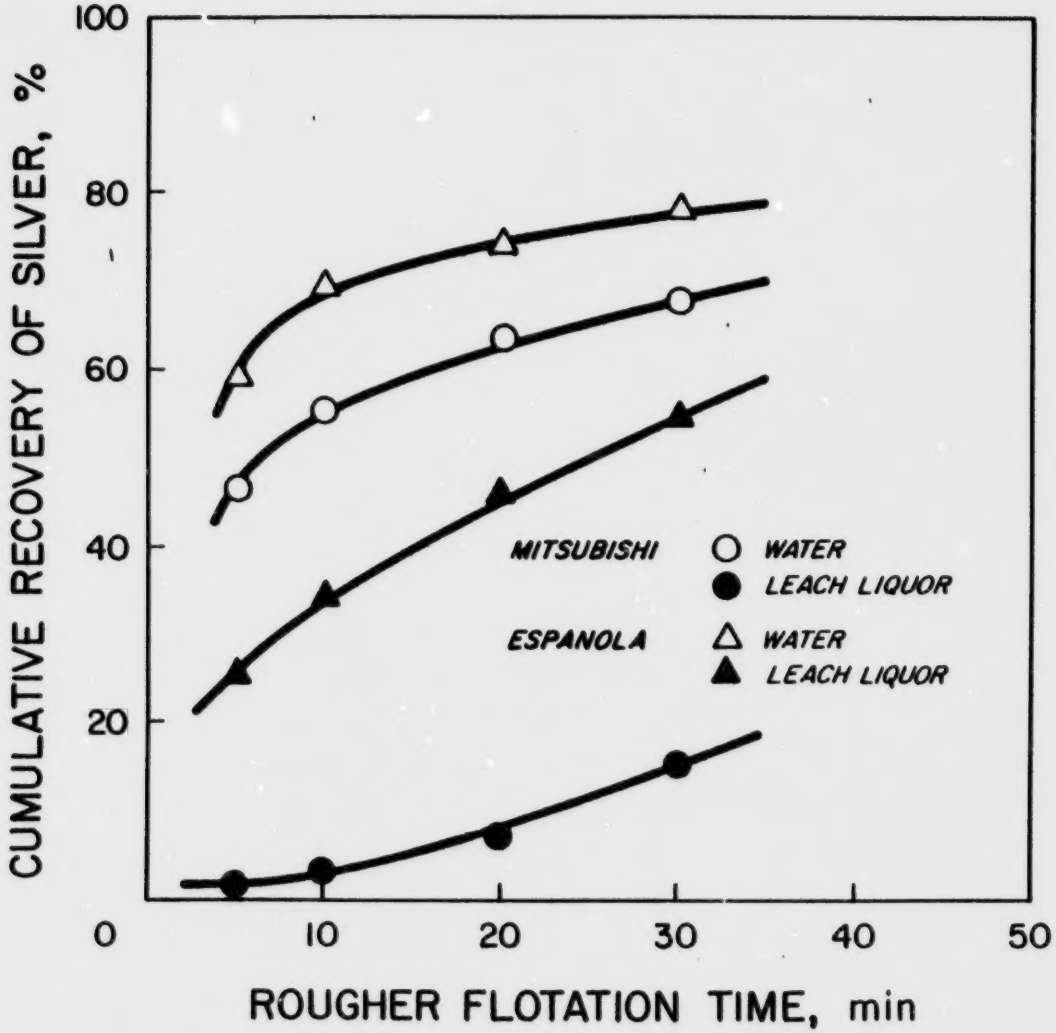

Figure 12 - Cumulative Silver Recovery Against Flotation Time

5.3.2.5 Effect of Residue Flocculants

As hydrometallurgical zinc plants normally thicken process leach residues with the aid of flocculants, the effect of flocculants on silver flotation was investigated for two flotation processes. A residue-water slurry at 25% solids was conditioned with the addition of 20 g/T each of Percol E-24 and Percol 351 in stages and then allowed to settle for 30 min. The flocculated pulp was then conditioned for flotation by the Espanola and Zhuzhou processes. Incremental samples of rougher froth were taken over 30 min. to evaluate the flotation response. The results are given in Table XXXVI, and cumulative silver recovery with flotation time is plotted in Figure 13, along with the results of previous tests without flocculation.

The Zhuzhou process after flocculation gave 3-5% reduction in the silver recovery, which may be considered as an experimental variation. However, the silver recovery was reduced by about 10% in the Espanola process.

5.3.3 Kidd Creek High Acid Leach Residue

Before evaluating the published processes for silver flotation from high acid leach residue, a series of preliminary tests was carried out to examine the flotation response of silver in (i) straight sulphide flotation, with and without sulphidization and (ii) anionic oxhydryl collector flotation. The results (Table XXXVII) show that at pH 3.0, silver recovery was about 25% to a concentrate assaying 0.46-0.65% Ag. At pH 8.0, the recovery increased to 31-42%, but the coflotation of other constituents reduced the grade to 0.27-0.32% Ag. Sulphidization did not improve the silver metallurgy. A high dosage of sodium sulphide (Test 217) produced a concentrate assaying 0.256% Ag with a silver recovery of 59.2%, however, the selectivity was poor as shown by flotation of 35.2% of the feed weight. Also anionic oxhydryl collector flotation resulted in poor silver recoveries and poor selectivity.

TABLE XXXVI

RESULTS OF FLOTATION TESTS USING FLOCCULATED NEUTRAL LEACH RESIDUE

FRACTION	WT %	ASSAYS, %			DISTRIBUTION, %		
		Ag	Pb	Zn	Ag	Pb	Zn
T-226. Espanola process, pH 5.0, Percol. E-24, 20 g/T, and 351, 20 g/T							
conc. 1	2.67	0.52	5.41	33.9	42.8	2.0	3.5
conc. 2	1.23	0.33	6.60	32.1	12.5	1.1	1.5
conc. 3	2.47	0.13	7.61	28.9	9.9	2.6	2.7
conc. 4	1.47	0.078	7.54	28.5	3.6	1.5	1.6
Tail	92.16	0.011	7.34	25.7	31.2	92.8	90.7
Heads	100.00	0.0324	7.29	26.1	100.0	100.0	100.0
T-225. Zhuzhou process pH 3.0, Percol. E-24 20 g/T, and 351, 20 g/T							
conc. 1	3.45	0.54	5.13	33.7	57.4	2.3	4.4
conc. 2	2.44	0.11	7.56	28.4	8.3	2.4	2.6
conc. 3	4.04	0.066	7.70	27.6	8.2	4.0	4.3
conc. 4	3.53	0.041	7.81	27.7	4.5	3.5	3.7
Tail	86.54	0.0081	7.87	25.9	21.6	87.8	85.0
Heads	100.00	0.0324	7.76	26.4	100.0	100.0	100.0

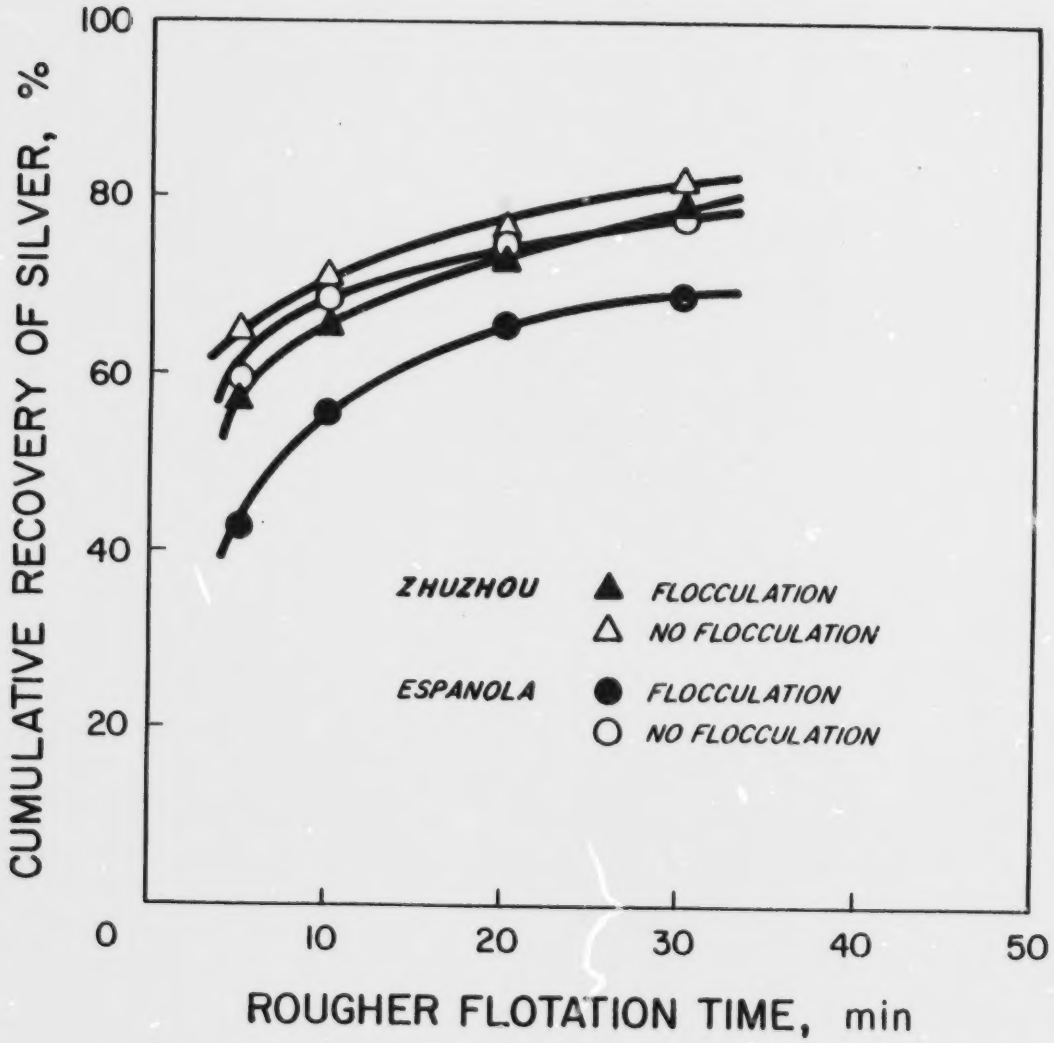

Figure 13 - Effect of Flocculation of Neutral Leach Residue Prior to Flotation

TABLE XXXVII

ROUGHER FLOTATION OF HIGH ACID LEACH RESIDUE

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/t	Sulphidization Time min.	Assay, % Ag			Silver Recovery %	wt. % of conc.
				Feed[2]	Conc.	Tail		
High Acid Leach Residue (0.13% Ag, 5.92% Pb)								
186[3]	3.0	-	-	0.151	0.647	0.12	25.4	5.9
188[3]	3.0	500	10	0.136	0.460	0.11	25.3	7.5
187[3]	8.0	-	-	0.140	0.320	0.10	42.0	18.4
189[3]	8.0	500	10	0.146	0.273	0.12	31.8	17.0
217[4]	3.0	15 kg/t	30	0.152	0.256	0.096	59.2	35.2
215[5]	3.0	-	-	0.155	0.233	0.136	29.6	19.6
216[6]	6.0	-	-	0.153	0.193	0.137	35.1	27.7

1. 250 g of residue was slurried at 15% solids, and conditioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with collector. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Feed assays were calculated from the assays and weights of the products.

3. Collector: 60 g/t R-3501 and 10 g/t AF 25.

4. Collector: 100 g/t R-3501 and 100 g/t R-3418A.

5. Collector: 400 g/t oleic acid (R-710).

6. Collector: 100 g/t alkyl sulphonate (R-899).

Mineralogical examination (Appendix IV) of the first rougher flotation concentrate sample cut during Test 186 showed that it consists of a jarosite-type compound (likely silver-bearing), sphalerite, elemental sulphur and possibly some lead sulphate together with minor to trace amounts of chalcopyrite, zinc ferrite, quartz, cassiterite and barite. Silver was detected either as ill-defined masses of selenium-bearing silver sulphide closely associated with minor Si or as $Ag_2(S,Se)$ particles in elemental sulphur-jarosite clusters.

The results of the flotation tests performed using published processes for floating silver and/or lead from the high acid leach residue are given in Table XXXVIII. All processes tested gave poor silver recoveries ranging from 29-46%. Those processes for the selective flotation of silver and lead to give separate concentrates (MET-MEX Penoles, Vieille Montagne and Dowa processes) did not give good lead recovery and did not differentiate significantly between the silver and lead in this residue sample.

5.3.4 Hematite Residue

The results of silver flotation from hematite using xanthate collector are shown in Table XXXIX. The silver recoveries to 10-min. rougher concentrates were only 8-25%, with and without sulphidization at pH 3 or 8. Pulp dispersion increased the silver recovery only slightly.

The literature review identified only two publications dealing with flotation of hematite residues; the Mitsubishi process (sulphation-roast-leach residue flotation with sulphide collectors at pH 3.5-4.0) and the Outokumpu process (prolonged sulphidization at elevated temperature in the prosence of silver sulphide and lead sulphide seed prior to flotation with sulphide collector). Therefore, a set of tests was carried out to investigate the flotation response of silver from the current hematite residue according to the Outokumpu process. The results are shown in Figure 14.

TABLE XXXVIII

ROUGHER FLOTATION OF HIGH ACID LEACH RESIDUE

PRODUCT	Weight %	Assays, %		Distribution, %	
		Ag	Pb	Ag	Pb
Test 198. MET-MEX Penoles Process					
Silver conc.	14.3	0.382	6.77	35.2	15.0
Lead conc.	18.7	0.138	7.54	16.7	21.7
Tails	67.0	0.111	6.10	48.1	63.3
Heads	100.0	0.155	6.46	100.0	100.0
Test 200. Vielle Montagne Process					
Silver conc.	16.6	0.272	6.84	29.0	17.5
Lead conc.	14.7	0.220	7.68	20.4	17.1
Tails	68.7	0.118	6.21	50.6	65.4
Heads	100.0	0.157	6.52	100.0	100.0
Test 201. Dowa Process					
Silver conc.	8.8	0.544	6.22	33.2	8.2
Lead conc.	25.0	0.137	8.88	22.9	33.3
Tails	66.2	0.112	5.90	51.9	58.5
Heads	100.0	0.143	6.67	100.0	100.0
Test 199. Asturiana Process					
Concentrate	22.2	0.328	7.23	46.4	25.2
Tails	77.8	0.108	6.12	53.6	74.8
Heads	100.0	0.157	6.37	100.0	100.0
Test 202. Tcho Process					
Concentrate	27.4	0.227	8.32	38.8	35.1
Tails	72.6	0.135	5.80	61.2	64.9
Heads	100.0	0.160	6.49	100.0	100.0

TABLE XXXIX

ROUGHER FLOTATION OF HEMATITE RESIDUE

Test No.	Pulp pH	$Na_2S \cdot 9H_2O$ g/t	Sulphidization Time min.	Assay, % Ag			Silver Recovery %	wt. % of conc.
				Feed[2]	Conc.	Tail		
Hematite Residue (0.019% Ag, 0.84% Pb)								
175	3.0	-	-	0.017	0.035	0.016	13.3	5.4
178	3.0	100	10	0.017	0.046	0.016	9.4	3.4
176	8.0	-	-	0.017	0.039	0.016	8.5	3.7
177	8.0	100	10	0.017	0.040	0.016	8.6	3.6
179[3]	8.0	-	-	0.016	0.034	0.014	25.4	12.4

1. 250 g of residue was slurried at 15% solids, and contitioned at the specific pH for 5 min. The pulp was further conditioned for 5 min. with 60 g/t R-350 and 10 g/t AF 25. Rougher flotation was conducted for 10 min. with the addition of frother. In sulphidization tests, sulphidization was done at the given pH before adding collector.

2. Feed assays were calculated from the assays and weights of the products.

3. 1 kg/t sodium hexametaphosphate was added during repulping.

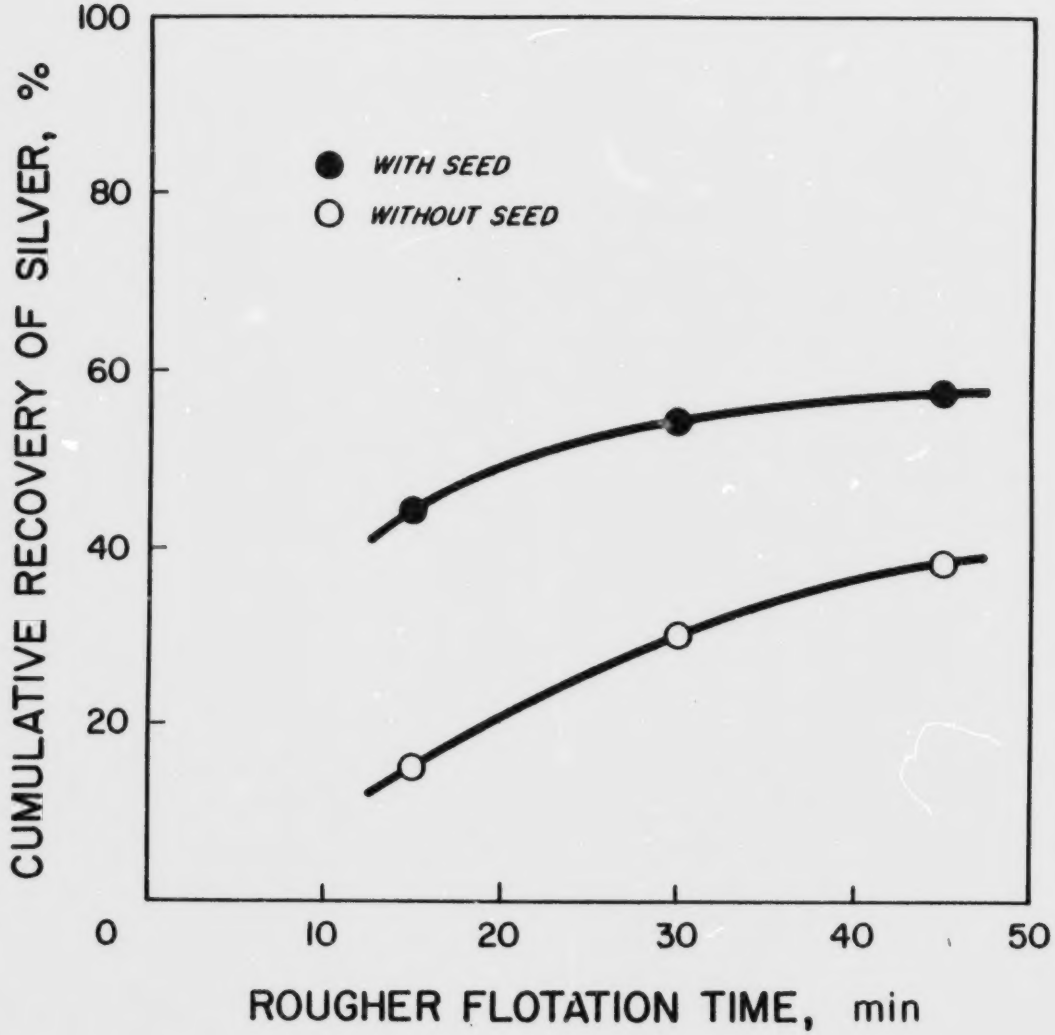

Figure 14 - Cumulative Silver Recovery from Hematite Residue Against Flotation Time (Outokumpu Process)

Silver recoveries (overall) of 58% and 38% were obtained in 45 min. of roughing, with and without seed, respectively. However, if the silver added as seed is deducted from the recovered silver, the net recovery of silver during flotation with seed was virtually identical to that without seed. Furthermore, it is believed that the somewhat higher silver recovery (38%) in this tests compared to the previous roughing tests is due to the longer flotation time, not prolonged sulphidization.

The reason for the poor silver recovery from hematite residue cannot be precisely defined at the present time. The results suggest that the silver may not be present as a distinct phase.

5.4 Conclusions

1. Flotation tests with zinc plant residues have resulted in widely varying silver recoveries (8-80%) depending on the type of residue. These results, together with the demonstrated ready floatability of silver compounds (metallic silver, silver chloride, silver sulphide) believed to occur in zinc plant residue, indicate that the successful flotation of silver from residue requires that the leach conditions be controlled to maintain silver in a liberated and floatable form. The formation of silver-bearing jarosites must be avoided.

2. The definition of suitable leach conditions for generation of a readily floatable residue is beyond the scope of the current program, and the "best" conditions may well vary from plant to plant depending upon the composition of the calcine, etc. The results obtained in the current study suggest that neutral or low acid leach residues be considered, but a high acid leach residue could be more attractive for those plants with an existing HAL circuit if conditions can be controlled to avoid jarosite formation.

3. Silver flotation from "suitable" fresh residues can be effected with conventional sulphide collectors. The flotation is slow, however, and long roughing times are required. Aged or oxidized residues may require more powerful collectors and/or the use of superficial sulphidization. There was no benefit identified, in this current study, through the use of large quantities of sulphide or prolonged slow sulphidization.

4. Work is required to determine (i) the effect of leach conditions and calcine composition on silver flotation from residue, (ii) the degree of residue washing required and (iii) the effect of flocculants used in residue thickening. The economies of residue flotation must also be assessed, including the impact of leach circuit modifications, additional liquid/solid separation requirements, plant water balance, zinc recovery, etc.

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APPENDIX I

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APPENDIX II

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APPENDIX III

DETAILS OF FLOTATION TESTWORK USING ZINC PLANT RESIDUES

TEST NO: 161 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: Rougher flotation at pH 3

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF 65			
Agitation	5	15	6.2								
Condition	5	15	3.0		6000						
Condition	5	15	3.0			60	10				
Float 1	5	10						20			
Float 2	5	10	3.5			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1	4.62	0.21	39.5			38.9	8.5		
Conc. 2	3.13	0.0916	26.1			11.5	3.8		
Tails	92.25	0.0134	20.3			49.6	87.7		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	7.75	0.162	34.1			50.4	12.3		

TEST NO: 162 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: Rougher flotation at pH 8.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-350	AF-25	AF-65			
Agitation	5	15	6.5								
Condition	5	15	8.0		4000						
Condition	5		8.0			60	10				
Float 1	5	10						20			
Float 2	5	10	7.6			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1	4.19	0.166	37.0			29.7	6.8		
Conc. 2	2.16	0.11	29.8			12.7	3.4		
Tails	93.20	0.0145	21.9			57.6	89.8		
Head (cal)	100.00	0.0234	22.74			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	6.80	0.146	34.2			42.4	10.2		

TEST NO: 163 SAMPLE: Prejarosite technology pond residue from CEZ, ground to minus 400 mesh

PURPOSE:

To find the effect of grinding, and float at pH 3.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF-65			
Grinding											
Agitation	5	~15	6.4								
Condition	5		3.0		6000						
Condition	5		3.0			60	10				
Float 1	5	~10						20			
Float 2	5		3.7			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	6.54	0.129				37.0			
Conc. 2	3.87	0.079				13.4			
Tails	89.59	0.0126				49.6			
Head (cal)	100.00	0.0228				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	8.41	0.110				50.4			

TEST NO: 165 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the superficial sulphidization before rougher flotation at pH 3.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65		
Agitation	5	∿15	6.3								
Condition	5		3.0		4000						
Sulphidization	10		3.0		1000	120					
Condition	5		3.0				60	10			
Float 1	5	∿10							20		
Float 2	5		3.7				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	5.07	0.158				34.8			
Conc. 2	2.77	0.072				8.7			
Tails	92.16	0.0141				56.5			
Head (cal)	100.00	0.0230				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	7.84	0.129				43.5			

TEST NO: 166 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of grinding and sulphidization before rougher flotation at pH 3.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65		
Grinding											
Agitation	5	~15	6.3								
Condition	5		3.0		4000						
Sulphidization	10		3.0		1000	110					
Condition	5		3.0				60	10			
Float 1	5	~10							20		
Float 2	5		3.6				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag		Zn		Ag		Zn	
Conc.1	7.49	0.1168		35.6		34.4		12.1	
Conc.2	3.72	0.0884		23.5		13.0		4.0	
Tails	88.79	0.0151		20.7		52.6		83.9	
Head (cal)	100.00	0.0254		21.9		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	11.21	0.1074	31.6			47.4	16.1		

TEST NO: 168 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of grinding and sulphidization before rougher flotation at pH 8.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65		
Grinding											
Agitation	5	∿15	6.4								
Condition	5		8.0		3500						
Sulphidization	10		8.0			110					
Condition	5		8.0				60	10			
Float 1	5	∿10							20		
Float 2	5		7.6				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %		DISTRIBUTION, %	
		Ag	Zn	Ag	Zn
Conc. 1	5.63	0.1547	34.9	37.5	9.1
Conc. 2	2.72	0.114	26.0	13.4	3.2
Tails	91.65	0.0124	20.7	49.1	87.7
Head (cal)	100.00	0.0232	21.7	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %		DISTRIBUTION, %	
		Ag	Zn	Ag	Zn
Conc. 1 and 2	8.35	0.1415	32.0	50.9	12.3

TEST NO: 175 SAMPLE: Hematite residue

PURPOSE: To find the flotation response at pH 3.0 with xanthate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF-65			
Agitation	5	~15	4.1								
Condition	5		3.0		200						
Condition	5					60	10				
Float 1	5	~10	3.0					20			
Float 2	5		3.3			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc 1	2.75	0.04				6.4			
Conc 2	2.71	0.031				4.9			
Tails	9454	0.016				86.7			
Head (cal)	100.00	0.017				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
conc. 1 and 2	5.46	0.0355				13.3			

TEST NO: 176 SAMPLE: Hematite residue

PURPOSE: To find the flotation response at pH 8.0 with xanthate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-350	AF-25	AF-65			
Agitation	5	∿15	4.2								
Condition	5		8.0		2400						
Condition	5					60	10				
Float 1	5	∿10	8.0					20			
Float 2	5		7.6			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	2.26	0.041				5.5			
Conc. 2	1.41	0.036				3.0			
Tails	96.33	0.016				91.5			
Head (cal)	100.00	0.0168				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	3.67	0.0391				8.5			

TEST NO: 177 SAMPLE: Rematite residue

PURPOSE: To find the flotation response at pH 8 after superficial sulphidization

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65		
Agitation	5	∿15	4.2								
Condition	5		8.0		2400						
Condition	10					100					
Condition	5		8.0				60	10			
Float 1	5	∿10							20		
Float 2	5		7.5				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	2.15	0.043				5.5			
Conc. 2	1.49	0.035				3.1			
Tails	96.35	0.016				91.4			
Head (cal)	100.00	0.0168				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	3.65	0.0397				8.6			

TEST NO: 178 SAMPLE: Hematite residue

PURPOSE: To find the flotation response at pH 3.0 after superficial sulphidization

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65		
Agitation	5	∿15	3.6								
Condition	5		3.0		200						
Condition	10					100					
Condition	5		3.0				60	10			
Float 1	5	∿10							20		
Float 2	5		3.1				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	2.07	0.051				6.2			
Conc. 2	1.38	0.039				3.2			
Tails	96.55	0.016				90.6			
Head (cal)	100.00	0.0170				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	3.45	0.0462				9.4			

TEST NO: 179 SAMPLE: Hematite residue

PURPOSE: To find the flotation response at pH 8.0 with dispersion

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	calgon*	R-350	AF-25	AF-65		
Agitation	5	∿15	4.1								
Condition	5		8.0		2400	1000					
Condition	5						60	10			
Float 1	5	∿10	8.0						20		
Float 2	5		7.5				20	5	20		

METALLURGICAL RESULTS

* calgon: Sodium Hexametaphosphate

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	5.50	0.0416				13.9			
Conc. 2	6.87	0.0276				11.5			
Tails	87.63	0.014				74.6			
Heads (cal)	100.00	0.0164				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	12.37	0.0338				25.4			

TEST NO: 181 SAMPLE: Neutral leach II residue, CEZ Pilot Plant

PURPOSE: To find the flotation response at pH 3.0 (natural pH) with dithiophosphate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					R-350	AF-25	AF-65				
Agitation	5	∿15	3.1								
Condition	5		3.0								
Condition	5				60	10					
Float 1	5	∿10					20				
Float 2	5		3.2		20	5	20				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag.		Zn		Ag		Zn	
Conc. 1	3.94	0.41		25.0		42.1		4.9	
Conc. 2	2.51	0.19		21.1		12.3		2.7	
Tails	93.55	0.018		19.8		45.1		92.4	
Head (cal)	100.00	0.0373		20.04		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	6.45	0.318	23.5			54.9	7.6		

TEST NO: 182 SAMPLE: Neutral leach residue, CEZ Pilot Plant

PURPOSE: To find the flotation response at pH 8.0 with dithiophosphate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-3501	AF-25	AF-65			
Agitation	5	∿15	3.2								
Condition	5		8.0		12kg/t						
Condition	5		8.0			60	10				
Float 1	5	∿10						20			
Float 2	5		8.1			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag		Zn		Ag		Zn	
Conc. 1	8.83	0.12		20.6		29.2		3.7	
Conc. 2	7.11	0.09		20.5		17.6		7.0	
Tails	84.06	0.023		20.9		53.2		84.3	
Head (cal)	100.00	0.0363		20.8		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	15.94	0.107	20.6			46.8	15.7		

TEST NO: 183 SAMPLE: Neutral leach residue, CEZ pilot plant

PURPOSE: To find the flotation response after sulphidization at pH 3.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	K-3501	AF-25	AF-65		
Agitation	5	∿15	3.1								
Condition	5		3.0								
Sulphidization	10		3.0		200	100					
Condition	5						60	10			
Float 1	5	∿10							20		
Float 2	5		3.1				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag		Zn		Ag		Zn	
Conc. 1	5.22	0.36		22.8		52.8		6.0	
Conc. 2	3.03	0.13		20.3		11.1		3.2	
Tails	91.75	0.014		19.5		36.1		90.8	
Head (cal)	100.00	0.0356		19.2		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	8.25	0.276	21.9			64.9	9.2		

TEST NO: 134 SAMPLE: Neutral leach residue, CEZ Pilot Plant

PURPOSE: To find the flotation response after sulphidization at pH 8.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$Na_2S \cdot 9H_2O$	R-3501	AF-25	AF-65		
Agitation	5	∿15	3.9								
Condition	5		8.0		8000						
Sulphidization	10		8.0		4000	100					
Condition	5		8.0				60	10			
Float 1	5	∿10							20		
Float 2	5		7.5				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag		Zn		Ag		Zn	
Conc. 1	14.51	0.12		19.4		46.6		14.5	
Conc. 2	6.83	0.096		18.1		17.6		6.3	
Tails	78.66	0.017		19.6		35.8		79.2	
Head (cal)	100.00	0.0373		19.5		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	21.34	0.112	19.0			64.2	20.8		

TEST NO: 185 SAMPLE: Neutral leach residue, CEZ pilot plant

PURPOSE: To find the flotation response after washing and long sulphidization period

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					$Na_2S \cdot 9H_2O$	R-350	AF-25	AF-65			
Agitation	5	15	3.1								
Filtration											
Repulp	5	~10	3.8								
Sulphidization	30		4.0		300						
Condition	5		4.0			60	10				
Float 1	5							20			
Float 2	5		4.1			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag		Zn		Ag		Zn	
Conc. 1	5.00	0.40		22.8		53.2		5.9	
Conc. 2	4.05	0.12		13.1		12.9		3.8	
Tails	90.95	0.014		19.3		33.9		90.3	
Head (cal)	100.00	0.0376		19.4		100.0		100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn			Ag	Zn		
Conc. 1 and 2	9.05	0.275	20.7			66.1	9.7		

TEST NO: 186 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response at pH 3.0 with dithiophosphate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-3501	AF-25	AF-65			
Agitation	5	∿15	2.4								
Condition	5		3.0		400						
Condition	5					60	10				
Float 1	5	∿10						20			
Float 2	5		2.8			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	2.85	0.87				16.4			
Conc. 2	3.08	0.44				9.0			
Tails	94.07	0.12				74.6			
Head (cal)	100.00	0.151				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	5.93	0.647				25.4			

TEST NO: 187 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response at pH 3.0 with dithiophosphate

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-3501	AF-25	AF-65			
Agitation	5	∿15	2.5								
Condition	5		8.0		40 kg/t						
Condition	5					60	10				
Float 1	5	∿10						20			
Float 2	5		7.6			20	5	20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb		Ag	Zn	Pb	
Conc. 1	14.76	0.30	5.96	6.34		31.5	14.8	14.7	
Conc. 2	3.67	0.40	6.08	6.69		10.5	3.8	3.8	
Tails	81.57	0.10	5.90	6.39		58.0	81.4	81.5	
Head (cal)	100.00	0.14	5.91	6.39		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb		Ag	Zn	Pb	
Conc. 1 and 2	18.43	0.32	5.96	6.41		42.0	18.6	18.5	

TEST NO: 188 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response after superficial sulphidization at pH 3.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$Na_2S \cdot 9H_2O$	R-3501	AF-25	AF-65		
Agitation	5	∿15	2.9								
Condition	5		3.0		4000						
Condition	10					500					
Condition	5		3.0				60	10			
Float 1	5	∿10							20		
Float 2	5		3.0				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	4.16	0.50				15.3			
Conc. 2	3.31	0.41				10.0			
Tails	92.53	0.11				74.7			
Head (cal)	100.00	0.136				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	7.47	0.46				25.3			

TEST NO: 189 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response after superficial sulphidization at pH 8.0

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$Na_2S \cdot 9H_2O$	R-3501	AF-25	AF-65		
Agitation	5	∿15	2.7								
Condition	5		8.0		40 kg/t						
Condition	10					500					
Condition	5		8.0				60	10			
Float 1	5	∿10							20		
Float 2	5		7.7				20	5	20		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1	9.86	0.29				19.6			
Conc. 2	7.16	0.25				12.2			
Tails	82.98	0.12				68.12			
Head(cal)	100.00	0.146				100.0			

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag				Ag			
Conc. 1 and 2	17.02	0.273				31.8			

TEST NO: 190 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with oxidized sulphide collector (Mercaptobenzothiazole) (Mitsubishi process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-404	AF-65				
Agitation	5	~15	3.6								
Condition	10		2.5		400						
Condition	10					500					
Float 1	5	~10					20				
Float 2	5										
Float 3	10						20				
Float 4	10		2.6								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.30	0.51	30.8	5.76	29.7	46.2	4.4	2.4	2.7
Conc. 2	2.02	0.16	26.6	6.19	33.4	8.9	2.3	1.6	1.8
Conc. 3	2.69	0.11	25.9	7.27	35.1	8.1	3.0	2.5	2.6
Conc. 4	2.36	0.075	25.4	7.40	35.1	4.8	2.5	2.2	2.3
Tails	89.63	0.013	22.8	8.04	36.8	32.0	87.8	91.3	90.6
Head (cal)	100.00	0.0364	23.3	7.89	36.4	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.30	0.51	30.8	5.76	29.7	46.2	4.4	2.4	2.7
Conc. 1 and 2	5.32	0.377	29.2	5.92	31.1	55.1	6.7	4.0	4.5
Conc. 1 to 3	8.01	0.287	28.1	6.37	32.4	63.2	9.7	6.5	7.1
Conc. 1 to 4	10.37	0.239	27.5	6.61	33.0	68.0	12.2	8.7	9.4

TEST NO: 191 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response after Cu activation and xanthate collector, (Espanola process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$CuSO_4$	R-350	AF-65			
Agitation	5	~25	3.8								
Condition	10		5.0		300						
Condition	10					200					
Condition	10						50				
Float 1	5	~15	5.0					20			
Float 2	5										
Float 3	10										
Condition	10					100					
Condition	10						50				
Float 4	10							20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	2.51	0.87	35.1	4.46	23.0	59.3	3.8	1.4	1.6
Conc. 2	1.78	0.20	27.3	6.14	32.2	9.7	2.2	1.4	1.6
Conc. 3	2.14	0.039	26.5	7.10	33.1	5.2	2.5	1.9	2.0
Conc. 4	2.38	0.061	26.1	7.40	34.3	4.0	2.7	2.2	2.3
Tails	91.19	0.0088	22.3	8.16	36.3	21.8	88.8	93.1	92.5
Head (cal)	100.00	0.0367	22.9	7.99	35.8	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	2.51	0.87	35.1	4.46	23.0	59.3	3.8	1.4	1.6
Conc. 1 and 2	4.29	0.592	31.9	5.16	26.8	69.0	6.0	2.8	3.2
Conc. 1 to 3	6.43	0.424	30.0	5.80	28.9	74.2	8.5	4.7	5.2
Conc. 1 to 4	8.81	0.326	29.0	6.23	30.4	78.2	11.2	6.9	7.5

TEST NO: 192 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with sulphidization (Zhuzhou process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3501	AF-65			
Agitation	5	∿25	3.6								
Condition	10		3.0		200						
Condition	10					100					
Condition	10						100				
Float 1	5	∿15	3.0					20			
Float 2	5										
Float 3	10										
Condition	5						50				
Float 4	10		3.0					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	2.40	0.98	35.9	3.96	22.0	65.0	3.8	1.2	1.5
Conc. 2	1.43	0.15	26.8	7.00	32.9	5.9	1.7	1.3	1.3
Conc. 3	2.71	0.069	25.9	6.22	33.7	5.2	3.2	2.1	2.5
Conc. 4	5.49	0.036	24.9	7.43	34.7	5.5	6.1	5.2	5.3
Tails	87.97	0.0076	21.6	3.05	36.6	18.4	85.2	90.2	89.4
Head (cal)	100.00	0.0362	22.3	7.85	36.0	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	2.40	0.98	35.7	3.96	22.0	65.0	3.8	1.2	1.5
Conc. 1 and 2	3.83	0.670	32.4	5.09	26.1	70.9	5.5	2.5	2.8
Conc. 1 to 3	6.54	0.421	29.7	5.56	29.2	76.1	8.7	4.6	5.3
Conc. 1 to 4	12.03	0.245	27.5	6.41	31.7	81.6	14.8	9.8	10.6

TEST NO: 193 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with long sulphidization at elevated temperature (without seed) (Outokumpu proc ss)

OPERATION	TIME min.	% SOLIDS	pH	TEMP. °C	REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3418	AF-65			
Agitation	5	25	3.4	50							
Condition	10		3.0		100	18,000					
Sulphidization	180			50							
Condition	5		3.0				200				
Float 1	15	15		45				20			
Condition	5						100				
Float 2	15			40				10			
Condition	5						100				
Float 3	15		3.2	35				10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	5.31	0.43	20.6	25.6	19.9	67.2	5.3	17.6	3.2
Conc. 2	2.72	0.16	21.1	19.6	26.8	11.7	2.5	6.3	2.0
Conc. 3	4.15	0.069	21.5	15.6	30.2	7.7	3.9	7.7	3.4
Tails	87.32	0.0057	23.1	6.62	38.0	13.4	88.3	68.4	91.4
Head (cal)	100.00	0.0342	22.3	8.45	36.3	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	5.31	0.43	20.6	25.6	19.9	67.2	5.3	17.6	3.2
Conc. 1 and 2	8.53	0.344	20.7	23.7	22.1	48.9	7.8	23.9	5.2
Conc. 1 to 3	12.68	0.254	21.0	21.0	24.7	86.6	11.7	31.6	8.6

TEST NO: 194 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of oxidized sulphide collector (Mercaptobenzothiazole) (Mitsubishi process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-404	AF-65				
Agitation	5	~25	6.4								
Condition	10		3.5		2000						
Condition	10		3.0		2000	500					
Float 1	5	~15					40				
Float 2	5										
Float 3	10						20				
Condition	10					200					
Float 4	10		3.5				20				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.94	0.230	40.0	0.38	23.4	37.9	8.0	2.6	2.4
Conc. 2	1.30	0.160	30.3	0.53	31.3	8.7	2.0	1.2	1.1
Conc. 3	2.75	0.081	25.8	0.63	36.9	9.3	3.6	2.9	2.7
Conc. 4	4.46	0.040	22.7	0.68	39.6	7.5	5.2	5.2	4.7
Tails	87.55	0.010	18.2	0.59	38.4	36.6	81.2	88.1	89.1
Head (cal)	100.00	0.0239	19.6	0.59	37.7	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.94	0.230	40.0	0.38	23.4	37.9	8.0	2.6	2.4
Conc. 1 and 2	5.24	0.213	37.6	0.42	25.3	46.6	10.0	3.8	3.5
Conc. 1 to 3	7.99	0.167	33.5	0.49	29.3	55.9	13.6	6.7	6.2
Conc. 1 to 4	12.45	0.122	29.6	0.56	33.0	63.4	18.8	11.9	10.9

TEST NO: 195 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of copper activation at pH 5 (Espanola process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$CuSO_4$	R-350	AF-65			
Agitation	5	~25	6.2								
Condition	10		5.0		1000						
Condition	10					100					
Condition	10						50				
Condition	1		5.0					20			
Float 1	5	~15									
Float 2	5							20			
Float 3	10							20			
Condition	5						50				
Float 4	10		5.2					20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.96	0.180	40.4	0.34	23.4	30.9	7.3	2.5	2.5
Conc. 2	1.66	0.110	28.2	0.57	34.1	7.9	2.1	1.7	1.5
Conc. 3	2.29	0.064	25.2	0.62	36.9	6.3	2.6	2.6	2.3
Conc. 4	2.74	0.037	23.6	0.65	38.4	4.5	3.0	3.4	2.8
Tails	89.35	0.017	20.8	0.54	38.0	50.4	85.0	89.8	90.9
Head (cal)	100.00	0.0230	21.9	0.54	37.3	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	3.96	0.180	40.4	0.34	23.4	30.9	7.3	2.5	2.5
Conc. 1 and 2	5.62	0.159	36.8	0.41	26.5	38.8	9.4	4.2	4.0
Conc. 1 to 3	7.91	0.132	33.5	0.47	29.5	45.1	12.0	6.8	6.3
Conc. 1 to 4	10.65	0.107	30.9	0.51	31.8	49.6	15.0	10.2	9.1

TEST NO: 196 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of superficial sulphidization at pH 3.0 (Zhuzhou process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3501	AF-65			
Agitation	5	~25	6.3								
Condition	10		3.0		2000						
Sulphidization	10					100					
Condition	10		3.0				100				
Float 1	5	~15						20			
Float 2	5							10			
Float 3	10		3.2					10			
Condition	5						50				
Float 4	10		3.8					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	4.09	0.25	43.1	0.30	20.8	39.0	8.9	2.3	2.3
Conc. 2	1.24	0.12	26.6	0.60	35.7	5.7	1.6	1.4	1.2
Conc. 3	1.51	0.061	24.4	0.81	38.8	3.5	1.8	2.3	1.6
Conc. 4	2.19	0.038	23.3	0.68	39.3	3.2	2.6	2.7	2.3
Tails	90.97	0.014	18.6	0.54	38.2	48.6	85.1	91.3	92.7
Head (cal)	100.00	0.0262	19.9	0.54	37.5	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	4.09	0.25	43.1	0.30	20.8	39.0	8.9	2.3	2.3
Conc. 1 and 2	5.33	0.22	39.3	0.37	24.2	44.7	10.5	3.7	3.5
Conc. 1 to 3	6.84	0.185	36.0	0.47	27.5	48.2	12.3	6.0	5.0
Conc. 1 to 4	9.03	0.149	32.9	0.52	30.3	51.4	14.9	8.7	7.3

TEST NO: 197 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of long sulphidization at high dosage of Na_2S and elevated temperature (without seeds) (Outokumpu process)

OPERATION	TIME min.	% SOLIDS	pH	TEMP. °C	REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3418	AF-65			
Agitation	5	~25	6.4	50							
Condition	5		3.0		3200						
Sulphidization	180		3.0	50		7500					
Condition	5			45			200				
Float 1	15	~15	3.0					10			
Condition	5			40			100				
Float 2	15		3.3					10			
Condition	5			37			100				
Float 3	15		3.6	35				10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	6.93	0.155	35.7	0.42	27.6	43.3	11.8	5.3	4.9
Conc. 2	3.47	0.062	22.6	0.67	39.3	8.7	3.7	4.2	3.5
Conc. 3	4.47	0.038	22.5	0.68	39.7	6.8	4.9	5.4	4.6
Tails	85.13	0.012	19.6	0.55	39.6	41.2	79.6	85.1	87.0
Head (cal)	100.00	0.0248	20.9	0.56	38.7	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	6.93	0.155	35.7	0.42	27.6	43.3	11.8	5.3	4.9
Conc. 1 and 2	10.40	0.124	31.3	0.50	31.5	52.0	15.5	9.5	8.4
Conc. 1 to 3	14.87	0.098	28.7	0.56	33.9	58.8	20.4	14.9	13.0

TEST NO: 198 SAMPLE: High acid leach residue

PURPOSE: To investigate the flotation response, two stage flotation (MET-MEX Penoles process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					R-3501	AF-65	R-899	NaOH			
Condition	∿10	∿25	2.2								
Condition	10				60						
Float 1	10	∿15				20					
Condition	10		5.5					15 kg/t			
Condition	5						200				
Float 2	25		6.0								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1 (silver conc.)	14.3	0.382	6.77			35.2	15.0		
Conc. 2 (lead conc.)	18.7	0.138	7.54			16.7	21.7		
Tail	67.0	0.111	6.10			48.1	63.3		
Head (cal)	100.0	0.155	6.46			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 199 SAMPLE: High acid leach residue

PURPOSE: To find the feasibility of floating silver and lead simultaneously (Asturiana process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					$Na_2S \cdot 9H_2O$	R-3501	AF-65				
Agitation	10	∿25	2.5								
Condition	20		3.0		4000						
Condition	10					60					
Float	25	∿15	3.1			20	20				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc.	22.2	0.328	7.23			46.4	25.2		
Tail	77.8	0.108	6.12			53.6	74.8		
Head (cal)	100.0	0.157	6.37			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 200 SAMPLE: High acid leach residue

PURPOSE: To find the feasibility of floating silver and lead concentrates separately (Vielle Montagne process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					R-242	2030	R-899	AF-65			
Agitation	10	~25	2.3								
Condition	20				60	50					
Float 1	30	~15									
Condition	10		2.5	50°C			200				
Float 2	10										

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1 (silver conc.)	16.6	0.272	6.84			29.0	17.5		
Conc. 2 (lead conc.)	14.7	0.220	7.68			20.4	17.1		
Tail	68.7	0.118	6.21			50.6	65.4		
Head (cal)	100.0	0.157	6.52			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 201 SAMPLE: High acid leach residue

PURPOSE: To find the feasibility of floating silver and lead concentrates separately (Dowa process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					R-3501	AMINE	AF-65				
Agitation	5	~25	2.2								
Condition	10				60						
Float 1	10	~15	2.2				20				
Condition	1					100					
Float	10		2.2								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1 (silver conc.)	8.8	0.544	6.22			33.2	8.2		
Conc. 2 (lead conc.)	25.0	0.137	8.88			22.9	33.3		
Tails	66.2	0.112	5.90			51.9	58.5		
Head (cal)	100.0	0.143	6.67			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 202 SAMPLE: High acid leach residue

PURPOSE: To find the feasibility of floating silver and lead simultaneously (Toho process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					GUM	R-3501	AMINE				
Agitation	10	~25	2.2								
Condition	5				500						
Condition	5					60					
Condition	5						200				
Float	20	~15	2.2								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc.	27.4	0.227	8.32			38.8	35.1		
Tail	72.6	0.135	5.80			61.2	64.9		
Head (cal)	100.0	0.160	6.49			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 203 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with cationic collector (Toho process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					Gum	R-3501	Amine	AF-65			
Agitation	10	∿25	3.7								
Condition	5		3.7		500						
Condition	5					40					
Condition	5		3.7				100				
Float 1	5	∿15						20			
Float 2	5										
Condition	3						50	10			
Float 3	10										
Float 4	10		3.8								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	20.00	0.0641	16.8	24.9	25.5	34.7	14.2	60.1	14.0
Conc. 2	6.51	0.0702	20.7	14.6	31.5	12.4	5.7	11.5	5.6
Conc. 3	15.02	0.0587	24.1	8.12	36.9	23.8	15.3	14.7	15.3
Conc. 4	2.33	0.0932	24.3	6.70	36.8	5.9	2.4	1.9	2.4
Tails	56.14	0.0153	26.3	1.75	40.5	23.2	62.4	11.8	62.7
Head (cal)	100.00	0.0370	23.6	8.29	36.3	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	20.00	0.0641	16.8	24.9	25.5	34.7	14.2	60.1	14.0
Conc. 1 and 2	26.51	0.0656	17.8	22.4	27.0	47.1	19.9	71.6	19.6
Conc. 1 to 3	41.53	0.0631	20.1	17.2	30.5	70.9	35.3	86.3	34.9
Conc. 1 to 4	43.86	0.0647	20.3	16.7	30.9	76.8	37.6	88.2	37.3

TEST NO: 204 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the flotation silver and lead in a rougher concentrate (Toho process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	Gum	R3501	Amine	AF-65		
Agitation	5	~25	5.8								
Condition	5		3.0		2000						
Condition	5					500					
Condition	5						40				
Condition	5		3.0					200			
Float 1	5	~15							10		
Float 2	5		3.3								
Float 3	10						40		10		
Float 4	10		4.0						10		

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	9.23	0.0609	24.6	1.08	35.1	21.2	10.8	18.2	8.6
Conc. 2	6.50	0.0861	28.9	0.77	31.1	21.2	8.9	9.1	5.4
Conc. 3	4.07	0.0720	25.8	0.71	35.0	11.1	5.0	5.3	3.8
Conc. 4	2.97	0.0606	23.7	0.76	37.1	6.8	3.4	4.1	2.9
Tails	77.23	0.0136	19.6	0.45	38.5	39.7	71.9	63.3	79.3
Head (cal)	100.00	0.0264	21.0	0.55	37.5	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	9.23	0.0609	24.6	1.08	35.1	21.2	10.8	18.2	8.6
Conc. 1 and 2	15.73	0.0713	26.4	0.95	33.4	42.4	19.7	27.3	14.0
Conc. 1 to 3	19.80	0.0714	26.3	0.90	33.7	53.5	24.7	32.6	17.8
Conc. 1 to 4	22.77	0.0700	25.9	0.88	34.2	60.3	28.1	36.7	20.7

TEST NO: 206 SAMPLE: Prejarosite technology pond residue from CEZ

PURPOSE: To investigate the effect of long sulphidization at high dose of Na_2S and elevated temperature in the presence of seeds (Outokumpu process)

OPERATION	TIME min.	% SOLIDS	pH	TEMP. °C	REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3418	AF-65			
Agitation	5	~25	5.3	50							
Condition	5		3.0		1500						
Sulphidization	180	25	3.0			7500					
Condition	5			50			200				
Float 1	15	~15	3.0	55				10			
Condition	5						100				
Float 2	15		3.4					10			
Condition	5			52			100				
Float 3	15		4.3	43				10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	6.83	0.36	36.8	5.22	21.9	61.9	11.5	39.8	4.1
Conc. 2	6.50	0.059	24.4	0.79	37.2	9.7	7.2	5.7	6.6
Conc. 3	5.02	0.046	24.6	0.79	37.0	5.8	5.7	4.4	5.1
Tails	81.65	0.011	20.2	0.55	37.6	22.6	75.6	50.1	84.2
Head (cal)	100.00	0.0397	21.8	0.90	36.5	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	6.83	0.36	36.8	5.22	21.9	61.9	11.5	39.8	4.1
Conc. 1 and 2	13.33	0.213	30.7	3.06	29.3	71.6	18.7	45.5	10.7
Conc. 1 to 3	18.35	0.167	29.1	2.44	31.4	77.4	24.4	49.9	15.8

TEST NO: 207 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with long sulphidization and seeds (Outokumpu process)

OPERATION	TIME min.	% SOLIDS	pH	TEMP. °C	REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3418	AF-65			
Agitation	5	~25	3.6	50							
Condition	5		3.0		200						
Sulphidization	180			50		96,000					
Condition	5			50			200				
Float 1	15	~15	3.0	50				20			
Condition	5						100				
Float 2	15			45				10			
Condition	5						100				
Float 3			4.9	40				10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	21.69	0.25	17.0	30.0	20.2	72.6	16.1	47.5	13.2
Conc. 2	10.50	0.075	22.1	18.8	28.8	10.5	10.2	14.4	9.1
Conc. 3	10.48	0.055	23.6	13.3	31.8	7.7	10.8	10.2	10.1
Tails	57.33	0.012	25.1	6.68	39.0	9.2	62.9	27.9	67.6
Head (cal)	100.00	0.0747	22.9	13.70	33.1	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Zn	Pb	Fe	Ag	Zn	Pb	Fe
Conc. 1	21.69	0.25	17.0	30.0	20.2	72.6	16.1	47.5	13.2
Conc. 1 and 2	32.19	0.193	18.7	26.4	23.0	83.1	26.3	61.9	22.3
Conc. 1 to 3	42.67	0.159	19.9	23.1	25.2	90.8	37.1	72.1	32.4

TEST NO: 215 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response with anionic oxhydryl collector

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-710	AF-65				
Agitation	5	∿15	2.2								
Condition	5		3.0		2400						
Condition						400					
Float 1	5	∿10									
Float 2	5		3.0								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1	9.72	0.216	7.17			13.6	10.8		
Conc. 2	9.88	0.251	6.97			16.0	10.6		
Tail	80.40	0.135	6.31			70.4	78.6		
Heads (cal)	100.00	0.155	6.46			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc.1 and 2	19.60	0.233	7.07			29.6	21.4		

TEST NO: 216 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response with anionic oxhydryl collector

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	R-899	AF-65				
Agitation	5	~15	2.5								
Condition	5		6.0		24 kg/t						
Condition	5					100					
Float 1	5	~10					20				
Float 2	5		6.0								
Float 3	5										

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1	14.3	0.162	7.48			15.2	16.7		
Conc. 2	6.6	0.202	7.32			8.7	7.5		
Conc. 3	6.8	0.251	6.91			11.2	7.3		
Tails	72.3	0.137	6.08			64.9	68.5		
Head (cal)	100.00	0.153	6.42			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1	14.3	0.162	7.48			15.2	16.7		
Conc. 1 and 2	20.9	0.175	7.43			23.9	24.2		
Conc. 1 to 3	27.7	0.193	7.30			35.1	31.5		

TEST NO: 217 SAMPLE: High acid leach residue

PURPOSE: To find the flotation response with sulphidization

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					$Na_2S \cdot 9H_2O$	R-3501	R3418	AF-65			
Agitation	10	15	2.2								
Condition	30		3.0		15 kg/t						
Condition	10					100	100				
Float 1	5	10	3.0					20			
Float 2	5										
Float 3	10					20	20				
Float 4	10		3.3								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1	11.28	0.322	7.97			23.8	13.8		
Conc. 2	7.04	0.266	7.70			12.3	8.3		
Conc. 3	10.30	0.217	7.76			14.6	12.3		
Conc. 4	6.62	0.195	7.50			8.5	7.6		
Tails	64.76	0.096	5.85			40.8	58.0		
Head (cal)	100.00	0.153	6.53			100.0	100.0		

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb			Ag	Pb		
Conc. 1	11.28	0.322	7.97			23.8	13.8		
Conc. 1 and 2	18.32	0.300	7.87			36.1	22.1		
Conc. 1 to 3	28.62	0.270	7.83			50.7	36.4		
Conc. 1 to 4	35.24	0.256	7.77			59.2	42.0		

TEST NO: 219 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the flotation response with xanthate collector at pH 3.0 (Binary process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF-65			
Agitation	5	∿25	6.2								
Condition	5		3.0		2500						
Condition	5					60	10				
Float 1	5	∿15	3.0					20			
Float 2	5										
Condition	3		3.7			30	5				
Float 3	10							10			
Float 4	10		4.0					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	5.35	0.16	0.49	38.6		42.1	5.6	10.2	
Conc. 2	1.31	0.06	0.65	26.6		4.9	2.4	2.2	
Conc. 3	0.95	0.044	0.65	26.9		1.9	1.2	1.2	
Conc. 4	2.80	0.027	0.62	26.4		3.4	3.4	3.3	
Tails	88.59	0.0219	0.50	20.8		47.8	87.4	83.1	
Head (cal)	100.00	0.0222	0.51	22.2		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	5.35	0.16	0.49	38.6		42.1	5.6	10.2	
Conc. 1 and 2	7.66	0.136	0.53	35.7		47.0	8.0	12.4	
Conc. 1 to 3	8.61	0.126	0.54	34.8		48.9	9.2	13.6	
Conc. 1 to 4	11.41	0.102	0.56	32.7		52.2	12.6	16.9	

TEST NO: 220 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the flotation response of two-stage flotation

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF-65	$Na_2S \cdot 9H_2O$	R3501	
Agitation	5	~25	6.2								
Condition	5		3.0		2000						
Condition	5					60	10				
Float 1	10	~15	3.0					20			
Condition	10								300		
Condition	5									40	
Float 2	10		3.8					20			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	6.53	0.15	0.25	41.7		44.5	3.4	12.0	
Conc. 2	3.73	0.030	0.46	26.4		6.5	3.6	4.3	
Tails	89.74	0.012	0.49	21.2		49.0	93.0	83.7	
Head	100.00	0.0220	0.47	22.7		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 221 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the flotation response with oxidized sulphide collector (two-stage flotation)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-404	AF-65	$Na_2S \cdot 9H_2O$	R-3501		
Agitation	5	~25	6.1								
Condition	5		3.0		2000						
Condition	10					500					
Float 1	10	~15	2.0				20				
Condition	10							100			
Condition	5								100		
Float 2	10		3.7				20				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	7.26	0.15	0.43	41.8		52.5	6.6	13.1	
Conc. 2	5.74	0.037	0.60	27.5		10.2	7.2	6.8	
Tails	87.00	0.0089	0.47	21.3		37.2	86.2	80.1	
Head	100.00	0.0208	0.47	23.1		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 222 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response with sulphidization (Binary process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9\ H_2O$	R3501	AF-25	AF-65		
Agitation	5	∿25	4.1								
Condition	5		3.0		200						
Condition	10		3.0			100					
Condition	5						60	10			
Float 1	5	∿15	3.0						20		
Float 2	5										
Condition	5						30	10			
Float 3	10								10		
Float 4	10		3.8								

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	3.59	0.52	5.37	34.2		60.0	2.4	4.6	
Conc. 2	1.91	0.11	7.14	27.9		6.7	1.7	2.0	
Conc. 3	3.86	0.053	7.73	27.4		7.2	3.8	4.0	
Conc. 4	2.90	0.041	7.45	30.1		3.8	2.7	3.3	
Tails	87.74	0.0079	8.02	26.1		22.3	89.4	86.1	
Head	100.00	0.0311	7.88	26.6		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	2.59	0.52	5.37	34.2		60.0	2.4	4.6	
Conc. 1 and 2	5.50	0.378	5.98	32.0		66.7	4.1	6.6	
Conc. 1 to 3	9.36	0.246	6.70	30.1		73.9	7.9	10.6	
Conc. 1 to 4	12.26	0.197	6.88	30.1		77.7	10.6	13.9	

TEST NO: 223 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response in the leach medium

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					$CuSO_4$	R-3501	AF-65				
Agitation	5	∿25	1.3								
Condition	10		1.6								
Condition	10				100						
Condition	10					100					
Float 1	5	∿15	1.6				20				
Float 2	5						10				
Condition	5					100					
Float 3	10						10				
Float 4	10		1.6				10				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	3.16	0.25	6.00	31.7		25.6	2.8	3.8	
Conc. 2	2.34	0.11	6.09	28.4		8.4	2.5	2.6	
Conc. 3	3.93	0.099	7.68	27.7		12.6	4.5	4.1	
Conc. 4	3.40	0.074	7.17	28.1		8.2	3.6	3.7	
Tails	87.17	0.016	6.65	25.7		45.2	86.6	85.8	
Head	100.0	0.0308	6.69	26.1		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	3.16	0.25	6.00	31.7		25.6	2.8	3.8	
Conc. 1 and 2	5.50	0.190	6.38	30.3		34.0	5.3	6.4	
Conc. 1 to 3	9.43	0.152	6.92	29.2		46.6	9.8	10.5	
Conc. 1 to 4	12.83	0.132	6.99	28.9		54.8	13.4	14.2	

TEST NO: 224 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the flotation response in the leach medium

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					R-404	AF-65	R-3501				
Agitation	5	~25	1.7								
Condition	10				500						
Float 1	5	~15				20					
Float 2	5					10					
Condition	5				200						
Float 3	10					10					
Float 4	10		1.7			10					

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	2.49	0.024	7.31	27.7		2.0	2.5	2.7	
Conc. 2	1.72	0.024	7.12	27.3		1.3	1.7	1.8	
Conc. 3	3.98	0.033	7.37	27.7		4.3	4.1	4.3	
Conc. 4	2.75	0.089	7.49	28.8		8.1	2.8	3.0	
Tails	89.06	0.0287	7.20	25.5		84.3	88.9	88.2	
Heads	100.0	0.0303	7.22	25.8		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 225 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigage the effect of flocculation prior to flotation

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					E-24	351	H_2SO_4	$Na_2S \cdot 9H_2O$	R-3501	AF-65	
Agitation	5	25	4.1								
Floculation	5				20						
Floculation	5					20					
Stand	30										
Condition	10		3.0				200				
Sulphidization	10							100			
Condition	10								60		
Float 1	5	~15	3.0							20	
Float 2	5									10	
Condition	5								60		
Float 3	10									10	
Float 4	10		3.3							10	

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	3.45	0.54	5.13	33.7		57.4	2.3	4.4	
Conc. 2	2.44	0.11	7.56	28.4		8.3	2.4	2.6	
Conc. 3	4.04	0.066	7.70	27.6		8.2	4.0	4.3	
Conc. 4	3.53	0.041	7.31	27.7		4.5	3.5	3.7	
Tails	86.54	0.0081	7.87	25.9		21.6	87.8	85.0	
Head	100.0	0.0324	7.76	26.4		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	3.45	0.54	5.13	33.7		57.4	2.3	4.4	
Conc. 1 and 2	5.89	0.362	6.14	31.5		65.7	4.7	7.0	
Conc. 1 to 3	9.93	0.241	6.77	29.9		73.9	8.7	11.3	
Conc. 1 to 4	13.46	0.189	7.04	29.3		78.4	12.2	15.0	

TEST NO: 226 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the effect of flocculation prior to flotation

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					E-24	351	NaOH	$CuSO_4$	R-350	AF-65	
Agitation	5	~25	4.1								
Floculation	5				20						
Floculation	5					20					
Stand	30		4.1								
Condition	5		5.0				100				
Condition	10							200			
Condition	10								100		
Float 1	5	~15	5.0							20	
Float 2	5									10	
Condition	5								50		
Float 3	10									10	
Float 4	10		5.0							10	

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	2.67	0.52	5.41	33.9		42.8	2.0	3.5	
Conc. 2	1.23	0.33	6.60	32.1		12.5	1.1	1.5	
Conc. 3	2.47	0.13	7.61	28.9		9.9	2.6	2.7	
Conc. 4	1.47	0.078	7.54	28.5		3.6	1.5	1.6	
Tails	92.16	0.011	7.34	25.7		31.2	92.8	90.7	
Head	100.00	0.0324	7.29	26.1		100.0	100.0	100.0	

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn		Ag	Pb	Zn	
Conc. 1	2.67	0.52	5.41	33.9		42.8	2.0	3.5	
Conc. 1 and 2	3.90	0.460	5.78	33.3		55.3	3.1	5.0	
Conc. 1 to 3	6.37	0.332	6.49	31.6		65.2	5.7	7.7	
Conc. 1 to 4	7.84	0.284	6.69	31.0		68.8	7.2	9.3	

TEST NO: 227 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the possibility of producing a cleaner concentrate with xanthate collector (Binary process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-350	AF-25	AF-65			
Agitation	5	∿30	6.1								
Condition	5		3.0		4000						
Condition	5					60	10				
Float	20	∿20						15			
Condition	3					30	5				
Float	10		3.7					10			
Cl 1 condition	5		3.0			10	5				
Cl 1 float	10		3.9					10			
Cl 2 condition	5		3.0			10	5				
Cl 2 float	8		3.5					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	2.59	0.37	0.06	62.5	5.9	41.2	0.3	7.6	0.4
Cl 2 tails	0.80	0.083	0.61	25.1	38.1	2.9	0.9	0.9	0.8
Cl 1 tails	6.64	0.033	0.62	25.9	37.7	9.4	7.8	8.1	7.0
Rougher tails	89.97	0.012	0.53	19.7	36.8	46.5	91.0	83.4	91.8
Heads	100.00	0.0232	0.52	21.3	36.1	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 228 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the possibility of producing a clean concentrate with oxide collector (Mitsubishi process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-404	AF-65				
Agitation	5	30	6.1								
Condition	5		3.0		6000						
Condition	5					500					
Float	20	20	3.0				20				
Condition	5					50					
Float	10						10				
Cl 1 condition	5		3.0			50					
Cl 1 float	10		3.6				10				
Cl 2 condition	5		3.0			50					
Cl 2 float	8		3.0				10				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	2.70	0.39	0.06	59.2	7.0	46.3	0.3	7.7	0.5
Cl 2 tails	0.58	0.107	0.62	25.4	37.4	2.8	0.6	0.7	0.6
Cl 1 tails	4.43	0.032	0.59	26.4	35.4	6.2	4.8	5.6	4.4
Rougher tails	92.29	0.011	0.56	19.4	36.8	44.7	94.3	86.0	94.5
Heads	100.00	0.0227	0.55	20.8	35.9	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 229 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the possibility of producing a clean concentrate with Cu activation and xanthate float (Espanola process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$CuSO_4$	R-350	AF-65			
Agitation	5	30	6.1								
Condition	5		5.0		1500						
Condition	10					100					
Condition	5						50				
Float	20	20	5.0					20			
Condition	5						25				
Float	10		5.4					10			
Cl 1 condition	5		5.0				10				
Cl 1 float	10							10			
Cl 2 condition	5		5.0				10				
Cl 2 float	8							10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	2.41	0.29	0.06	60.1	6.8	32.0	0.3	6.9	0.5
Cl 2 tails	0.65	0.17	0.63	25.6	35.8	5.0	0.7	0.8	0.6
Cl 1 tails	5.89	0.033	0.58	29.7	31.9	8.9	6.2	8.3	5.2
Rougher tails	91.05	0.013	0.56	19.4	36.9	54.1	92.8	84.0	93.7
Heads	100.00	0.0219	0.55	21.0	35.9	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 230 SAMPLE: Prejarosite technology pond residue

PURPOSE: To investigate the possibility of producing a clean concentrate with sulphidization-flotation (Zhuzhou process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3501	AF-65			
Agitation	5	30	6.2								
Condition	10		3.0		4500						
Condition	10					100					
Condition	10						100				
Float	20	20	3.0					20			
Condition	5						50				
Float	10							10			
Cl 1 condition	5		3.1				10				
Cl 1 float	10		4.0					10			
Cl 2 condition	5		3.0				10				
Cl 2 float	3		4.0					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	2.35	0.31	0.08	53.6	8.9	41.3	0.5	7.9	0.7
Cl 2 tails	2.10	0.040	0.62	24.8	37.0	4.0	3.1	2.5	2.2
Cl 1 tails	10.06	0.021	0.63	24.7	37.1	10.0	14.8	11.8	10.6
Rougher tails	84.99	0.011	0.41	19.3	35.8	44.2	81.8	77.8	86.5
Heads	100.00	0.0211	0.43	21.1	35.2	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			

TEST NO: 231 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the possibility to obtain a high grade silver concentrate, oxidized sulphide collector (Mitsubishi process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	R-404	AF-65				
Agitation	5	30	4.1								
Condition	10		3.0		200						
Condition	10					500					
Float 1	20	20					20				
Condition	5		3.0			100					
Float 2	10		4.1				10				
Cl condition	5		3.0			40					
Cl float	10						10				
Cl 2 condition	5		3.0			40					
Cl float	8						10				

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	1.12	1.75	1.07	45.8	11.3	63.3	0.1	2.2	0.4
Cl 2 tails	1.23	0.098	7.28	29.5	32.0	3.8	1.1	1.5	1.2
Cl 1 tails	8.56	0.032	5.87	32.1	29.9	8.8	6.2	11.5	7.5
Rougher tails	89.09	0.0084	8.42	22.6	34.7	24.1	92.6	84.8	90.9
Head	100.00	0.0311	8.11	23.8	34.0	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	1.12	1.75	1.07	45.8	11.3	63.4	0.1	2.2	0.4
Cl conc. + Cl 2 tails	2.35	0.388	4.01	37.3	22.1	67.1	1.2	3.7	1.6
Rougher conc.	10.91	0.216	5.53	33.2	28.2	75.9	7.4	15.2	9.1

TEST NO: 232 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the possibility of obtaining a high grade silver concentrate, Cu-activation and xanthate float (Espanola process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					NaOH	$CuSO_4$	R-350	AF-65			
Agitation	5	~30	4.1								
Condition	10		5.0		200						
Condition	10					100					
Condition	10						50				
Float 1	20	~20						20			
Condition	5						20				
Float 2	10		5.0					10			
Cl 1 condition	5		5.0				10				
Cl float	10							10			
Cl 2 condition	5						10				
Float	8		5.5					10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	1.26	1.93	0.83	45.6	9.2	70.8	0.1	2.5	0.3
Cl 2 tails	0.91	0.17	4.97	32.8	28.2	4.5	0.6	1.3	0.7
Cl 1 tails	6.64	0.04	7.15	28.9	32.3	7.7	6.2	8.3	6.3
Rougher tails	91.19	0.0064	7.84	22.2	34.7	17.0	93.1	87.9	92.7
Heads	100.00	0.0344	7.68	23.0	34.2	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	1.26	1.93	0.83	45.6	9.2	70.8	0.1	2.5	0.3
Cl conc. + Cl 2 tails	2.17	1.195	2.56	40.3	17.1	75.3	0.7	3.8	1.0
Rougher conc.	8.81	0.324	6.02	31.7	28.6	83.0	6.9	12.1	7.3

TEST NO: 233 SAMPLE: Neutral leach residue, pilot plant

PURPOSE: To investigate the possibility of obtaining a high grade silver concentrate, superficial sulphidization (Zuhzhou process)

OPERATION	TIME min.	% SOLIDS	pH		REAGENTS, g/t						
					H_2SO_4	$Na_2S \cdot 9H_2O$	R3501	AF-65			
Agitation	5	~30	4.1								
Condition	10		3.0		200						
Condition	10		3.0			100					
Condition	10						100				
Float 1	20	~20						20			
Condition	5						50				
Float 2	10		3.4					10			
Cl 1 condition	10		3.0				10				
Cl float	10							10			
Cl 2 condition	10		3.0				10				
Cl 2 float	7							10			

METALLURGICAL RESULTS

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl conc.	1.28	1.66	0.85	48.0	8.9	67.4	0.1	2.5	0.3
Cl 2 tails	1.02	0.152	6.27	30.5	30.2	4.9	0.8	1.3	0.9
Cl 1 tails	9.66	0.033	7.36	28.0	32.8	10.0	8.6	11.0	9.3
Rougher tails	88.04	0.0064	8.53	23.6	14.6	17.7	90.5	85.2	89.5
Heads	100.00	0.0317	8.30	24.5	34.1	100.0	100.0	100.0	100.0

CALCULATED GRADES AND RECOVERIES

FRACTION	wt %	ASSAY, %				DISTRIBUTION, %			
		Ag	Pb	Zn	Fe	Ag	Pb	Zn	Fe
Cl Conc.	1.28	1.66	0.85	48.0	8.9	67.4	0.1	2.5	0.3
Cl conc. + Cl 2 tails	2.30	0.994	3.24	40.3	18.3	72.3	0.9	3.8	1.2
Rougher conc.	11.96	0.218	6.57	30.4	30.0	82.3	9.5	14.8	10.5

APPENDIX IV

MINERALOGICAL EXAMINATION OF SILVER FLOTATION CONCENTRATES AND ZINC LEACH RESIDUES

Energy, Mines and Resources Canada
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CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

A MINERALOGICAL EXAMINATION OF SILVER FLOTATION CONCENTRATES MADE FROM ZINC LEACH RESIDUES

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A MINERALOGICAL EXAMINATION OF SILVER FLOTATION CONCENTRATES MADE FROM ZINC LEACH RESIDUES

by

J.E. Dutrizac* and T.T. Chen*

ABSTRACT

Two neutral leach residues and one high acid leach residue from zinc processing circuits were subjected to flotation to produce three silver concentrates. A mineralogical investigation was carried out to characterize the feeds and products and to elucidate the mineral forms of silver. Only one silver occurrence was observed in the neutral leach residues and this was as Ag_2S coatings on sphalerite. Silver sulphide-coated sphalerite was also present in the high acid leach residue although the major occurrence of silver in that feed was a sulphur-silica gel-like material. Silver-bearing jarosite is also a probable silver carrier in that feed. The concentrate produced from the high acid leach residue contained abundant silver as ill-defined masses of $Ag_2(S,Se)$ bearing some resemblence to the gel-like material in the original feed and as tiny $Ag_2(S,Se)$ inclusions in elemental sulphur-jarosite clusters. Silver is also probably contained in the jarosite in this concentrate. Abundant silver was evident in the concentrate prepared from the neutral leach residue made in the pilot run; many if not

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most of the sphalerite grains in this concentrate were rimmed with a Pb-Ag sulphide, possibly also containing some Zn and iron. The flotation concentrate made from the neutral leach residue in the CEZ storage pond contained sphalerite rimmed with Ag_2S and $(Cu,Ag)_2S$; inclusions of these sulphides were also seen in some of the larger sphalerite grains.

INTRODUCTION

Silver is present in minor amounts in most commercial zinc concentrates. During processing by the roast-leach-electrowin method, most of the silver reports in the various leach residues; virtually no silver dissolves in the sulphuric acid-zinc sulphate leaching medium despite the relatively high solubility of both Ag_2SO_4 and AgCl in such solutions (1,2). The recovery of silver from the leach residues has traditionally been poor and erratic, with the best success being achieved by the recycle of the residues into a lead smelting circuit coupled with a zinc slag fuming furnace. The use of this practice is, however, clearly limited to those few zinc plants adjacent to conventional lead smelters, and may not be at all possible with the new generation of lead flash smelting furnaces. The recovery of silver values by alternate technologies such as froth flotation would clearly be more universally applicable and could offer processing advantages over the lead smelter route.

In view of the general desirability of developing alternate methods for recovering silver from zinc residues and the recent success of flotation at such installations as Vieille-Montagne's Balen zinc plant, CANMET issued a contract to the Noranda Research Centre to evaluate flotation methods for the recuperation of silver from Canadian zinc plant leach residues. As part of that contract, Noranda Research produced flotation concentrates from both fresh and impounded neutral leach residues and from a high acid leach residue. The purpose of the current CANMET investigation was to complement the corporate contract work by conducting a detailed mineralogical examination of these materials, with special emphasis on their silver mineralogy.

EXPERIMENTAL

Three residues and three flotation concentrates were provided for study. A description of the six samples together with some limited chemical data supplied by the company is presented in Table 1. The samples were reportedly well washed to eliminate soluble salts and were subsequently air dried. All samples were examined "as-received" without any further treatment.

In addition to classical ore microscopy, a variety of mineralogical techniques was used to examine the leach residues and, especially, the flotation concentrates. All samples were examined by X-ray powder diffraction methods to identify the major phases present. A MAC 400 electron microprobe was used in conjunction with the SEM-EDX unit to help locate regions rich in silver. These regions were then subjected to detailed study on the scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) and backscattered electron imagery. Although most of the studies were done using full polished sections of the various materials, some work was also carried out on the loose concentrates to ensure that silver was not being lost during polishing.

RESULTS AND DISCUSSION

4971 - NEUTRAL LEACH RESIDUE FROM THE CEZ STORAGE POND

X-ray diffraction analysis showed this material to consist of zinc ferrite, sphalerite and quartz together with a trace of hematite.

Microscopic examination (Figure 1) indicated relatively coarse composite grains cemented together by an iron hydroxide material which is apparently amorphous and may be mixed with a Fe-Zn sulphate. The fine-grained iron hydroxide phase (medium to dark grey) consists of major iron together with

Table 1 - A description of the six samples provided for mineralogical study

Identifier Number	Description	Chemical Composition (wt.%)				Silver Recovery** Into Concentrate (%)
		Ag	Zn	Pb	Se*	
4971	Neutral leach residue from the storage pond of Canadian Electrolytic Zinc; this residue was several years old.	0.021	20.4	0.60	-	n.a.
4973	Neutral leach residue from a pilot plant run conducted by Noranda Research.	0.037	22.1	8.33	-	n.a.
4976	High acid leach residue from Kidd Creek Mines, Timmins.	0.13	5.71	5.92	-	n.a.
4987	T-186C, flotation concentrate produced from high acid leach residue.	0.87	-	-	0.35	25%
5009	T-192C, flotation concentrate produced from pilot plant neutral leach residue.	0.98	35.7	3.96	0.04	65%
5028	T-196C, flotation concentrate produced from the neutral leach residue in the CEZ storage pond.	0.25	43.1	-	0.08	44%

* CANMET analysis

** The concentrate from each flotation test was obtained in four fractions; the reported silver recovery applies to only the one (of four) fraction examined.

minor amounts of zinc and traces of Mn, Cu, Al and SO_4. This phase is abundant but does not give an X-ray diffraction pattern; it is presumably the ferric hydroxide phase formed at moderately high pH values in the neutral leaching step. Zinc ferrite is abundant both as cellular masses (large central light grey mass) and as compact grains (light grey) in the groundmass. A number of compact grains of hematite are also evident, and these are a slightly darker shade of grey than the zinc ferrite particles. The large centre-right composite grain contains about equal amounts of hematite and zinc ferrite particles. The hematite tends to be pure whereas the ferrite phase contains traces of manganese.

Figure 2 shows the detailed structure of one of the large composite grains cemented together by the iron hydroxide phase. The fibrous grain at the lower-left is an iron silicate containing minor amounts of Al and traces of Zn, Mn, Mg and Ca; a number of grains of Fe-Al silicates and Fe-Al-Mg silicates were identified in this residue. The porous, light grey grain at the lower-centre of the photo is hematite, but most of the other compact, light-grey grains are zinc ferrite. Figure 3 illustrates another field of view of one of the composite grains which is again cemented together by an iron hydroxide phase. In this photograph, the dark grey central grain is quartz and the medium grey oval grains at the lower-centre-left are manganese oxide (MnO_2?) containing minor Fe and traces of Cu and Zn. The large light grey grain at the centre-left is zinc ferrite containing a trace of copper.

Other phases detected during the examination of this residue included pyrite, sphalerite and a Zn-Fe sulphate. No silver minerals or silver-bearing phases were found in this residue which contained 210 ppm Ag.

4973 - NEUTRAL LEACH RESIDUE FROM THE PILOT PLANT RUN

X-ray diffraction analysis showed this residue to consist mostly of zinc ferrite and lead sulphate.

Microscopically, this neutral leach residue was considerably different from the pond residue examined above in that it is more fine grained and is entirely lacking in the large aggregates cemented by iron hydroxide. Figure 4 presents a general view of this leach residue, and it is clear that it consists mostly of particles less than 10 μm although a few larger grains are also evident. Near the centre of the field is a large medium grey grain of iron-bearing sphalerite and similar grains were evident in most of the fields examined. The slightly darker, tiny compact grains forming the majority of the field are zinc ferrite. The light grey to white particles are lead sulphate, and these are generally <5 μm although a large (15 μm) $PbSO_4$ spherical cluster is evident in the lower-left corner. The somewhat nebuluous medium grey mass associated with this $PbSO_4$ cluster is a zinc-iron sulphate containing some lead and traces of Si, Cu and Mn. Trace amounts of hematite, magnetite and pyrite were also seen in this residue.

Figure 5 shows the detailed structure of the pilot plant neutral leach residue, and this figure is of some significance since it illustrates the only silver-bearing grain detected. In this field, the small (<10 μm) medium grey compact grains are zinc ferrite and the small white particles are $PbSO_4$. The large central grain is iron-bearing sphalerite, and the grey zone (~2 μm) at the bottom tip of the sphalerite grain is Ag_2S. Clearly, this one silver particle is not adequate to account for all of the 370 ppm Ag contained in this residue, but it does indicate how silver occurs in this material.

4976 - HIGH ACID LEACH RESIDUE

X-ray powder diffraction analysis showed this residue to consist predominantly of a jarosite-type compound, lead sulphate and sphalerite.

Microscopic study indicated the residue to be extremely fine grained, with most particles being <10 μm in diameter. Figure 6 presents a general view of the residue and the fine-particle sizes are readily discernible. In this photo, the medium grey, fine grained mass constituting the majority of the field of view is a jarosite-type compound (likely a Pb-K-Zn-bearing sodium jarosite), and the white grains are sphalerite. The medium, compact grains (∿10 μm) are hematite or zinc ferrite, often intimately associated with the jarosite. Study of this residue also indicated minor to trace amounts of quartz and sphalerite (∿3 μm) as well as traces of chalcopyrite, pyrite, gypsum, a manganese sulphide (?) and a tin sulphide.

Two forms of silver were identified in this residue and a third (trace Ag substitution in the jarosite-type compounds) likely exists as well (3). The major occurrence of silver was as a poorly defined gel-like layer, commonly situated at the edge of a hole or pit or at the polished surface. Figure 7a illustrates the general morphology of these gel-like layers, and Figure 7b shows the relative silver (AgL_α X-ray map) distribution in the gel. The gel-like phase (central white to light grey mass in Figure 7a) consistently indicated major sulphur and silicon together with minor Ag and Fe, and traces of Zn, Pb, Sn and Al. It is felt that the gel-like phase consists essentially of elemental sulphur and a silica gel; the method by which silver is incorporated in such material is not known but it is likely present as fine Ag_2S particles. The second identified form of silver was thin coatings of Ag_2S on the edges of iron-bearing sphalerite grains. The silver sulphide always contained minor to trace amounts of Pb as well as occasional traces

of Se. Unfortunately, the Ag_2S layer was too thin and too intimately associated with other phases for a definitive electron microprobe analysis. The amounts of silver observed, when considered in the light of the probable Ag content of the jarosite phase, are likely sufficient to account for the 1,300 ppm Ag in this residue.

4987 - FLOTATION CONCENTRATE FROM THE HIGH ACID LEACH RESIDUE

X-ray powder diffraction analysis of this concentrate indicated a jarosite-type compound, sphalerite, elemental sulphur and possibly some lead sulphate. The presence of elemental sulphur was confirmed by X-ray diffraction analysis of grains removed from the powder mounts.

Microscopic examination of polished sections of this flotation concentrate indicated a very fine-grained texture with most particles being <2 μm in size. Figure 8 illustrates a general view of this material and clearly shows the fine grain size of most of the particles. The majority of the field of view (medium grey) consists of jarosite-type compounds showing major iron and sulphur together with minor amounts of Na, Pb, K and Zn, and traces of Ag, Si, Al, Se, Ba and Sn. The jarosite-type compound is likely a Pb-K-Zn-bearing sodium jarosite. It is felt that the Ag, Al and Se are associated with the jarosite but that the other elements are present as discrete impurity grains (3). The fine particle sizes in this material, do not permit a definitive clarification of the elements substituted in the jarosite as opposed to those elements intimately mixed with the jarosite phase as tiny impurity grains. A previous study (3) has, however, shown Ag substitution in the jarosite contained in a similar residue from Kidd Creek Mines. The bright white, compact grains in Figure 8 are iron-bearing sphalerite, and the spherical black spots (e.g., upper right corner) are elemental sulphur associated with jarosite.

Elemental sulphur does not polish particularly well and it commonly lifts out of the section during polishing. To try to show the elemental sulphur better, a loose powder mount of this concentrate was prepared, and this is shown in Figure 9. The light grey spherical clusters (2-50 μm) are elemental sulphur containing traces of Fe, Zn and Si. The sulphur clusters are frequently intimately mixed with jarosite-type compounds. The abundance of the sulphur clusters as shown in the loose powder mount would not be inferred from an examination of the polished section of this flotation concentrate (Fig. 8). Figure 10 shows the detailed structure of one of the sulphur-jarosite clusters, and it is evidently porous and composed of a number of still smaller particles.

Other compounds observed during the general study of this concentrate, in either polished section or loose powder mounts, include minor amounts of chalcopyrite and zinc ferrite as well as traces of quartz, SnO_2 (cassiterite), hematite and $BaSO_4$ (barite).

This concentrate contains 0.87% Ag and over 25 separate Ag-bearing grains were examined during the study of this material. Two (but possibly closely related) forms of silver were identified and it is also likely that silver is substituted to a limited extent in the jarosite crystals. Analysis of masses of jarosite crystals (individual crystals are too small for individual analysis) indicated traces of silver but, of course, there is no way of knowing for sure that the silver is actually incorporated in the Pb-K-Zn-bearing sodium jarosite lattice.

One major type of occurrence of silver was as ill-defined masses of a silver sulphide phase closely associated with minor Si and traces of Fe, Zn, Pb and Al. This material was always associated with a hole or the edge of a hole and bore some resemblence to the gel-like particles detected in the high

acid leach residue. Selenium was always closely associated with silver in this mode of occurrence and the actual silver compound is likely $Ag_2(S,Se)$. Figure 11 illustrates one of these masses of $Ag_2(S,Se)$ where the silver phase is the large (~25 μm) medium grey mass showing a central hole. The ill-defined mass shows major sulphur and silver, minor silicon and traces of Fe, Se and Zn. The mass of silver sulphide is surrounded by fine crystals of jarosite (medium grey) and small grains of sphalerite (white).

Figure 12a illustrates another of these $Ag_2(S,Se)$ masses which is clearly associated with a large crack. Figure 12b illustrates the relative concentration of silver (AgL_α X-ray map). The silver-bearing region consisted of $Ag_2(S,Se)$ with minor iron and traces of Zn, Si, Pb and Al. The small rings (white) in the lower-right quadrant consist mostly of sulphur containing minor silver and silicon together with traces of Fe, Zn, Al, Pb and Se. These sulphur rings seem to be joined to the central mass of $Ag_2(S,Se)$. Figure 13 illustrates the detailed structure of another $Ag_2(S,Se)$ mass. It is evident that the silver sulphide is lacking in crystal features and that it is rough and irregular; it has the features of a precipitate.

The second major type of silver occurrence was as tiny $Ag_2(S,Se)$ inclusions in the elemental sulphur-jarosite clusters. Examination of the sulphur in the loose powder mounts (Fig. 9) commonly indicated $Ag_2(S,Se)$ particles as is evident in Figures 14 and 15 where the sulphur-jarosite masses are the medium grey phase and the $Ag_2(S,Se)$ is white. The silver sulphide particles in the sulphur-jarosite masses are ~2 μm in size and also seem to be selenium-bearing. The sulphur-jarosite masses contain minor Si and Fe as well as trace quantities of Zn, Pb, Al, Ba and Sn. Chlorine was occasionally detected with Ag in the loose powder mounts, but this is felt to originate

from the mounting glue used to attach the powder to the stage and not to be due to silver chloride. Silver sulphide rimmed sphalerite was present in the leach residue, but was not seen in this concentrate which contains only 25% of the silver in the original feed (Table 1).

5009 - FLOTATION CONCENTRATE FROM THE PILOT PLANT NEUTRAL LEACH RESIDUE

The concentrate prepared from the pilot plant neutral leach residue was shown by X-ray powder diffraction analysis to consist of major sphalerite and zinc ferrite together with a trace amount of quartz.

Microscopic study of this concentrate showed it to consist (Figure 16) of major iron-bearing sphalerite as both fine and coarse grains (light grey) in a matrix of fine-grained zinc ferrite (dark grey). Also present were occasional grains of quartz, pyrite and chalcopyrite. Most of the sphalerite grains are rimmed by a sulphide phase containing Ag and Pb together with lesser amounts of Fe and Zn.

This concentrate contains 0.98% Ag and abundant silver was detected mineralogically in this sample. The silver seemed to occur exclusively as a compact to diffuse rim on the sphalerite grains, especially the medium to small size grains ($\leq$10 µm); most of these smaller particles were rimmed by the Ag-bearing sulphide and many of the larger sphalerite grains were likewise coated. Figure 17 shows a small and a medium sized grain of iron-bearing sphalerite (medium grey) completely rimmed by the Ag-bearing sulphide (white to light grey). The sulphide rim varies in thickness from $\sim$1 µm to several microns. Figure 17b presents a AgL_{α} X-ray map showing the relative distribution of silver about the two grains, and Figure 17c illustrates the corresponding X-ray map (PbL_{α}) for lead. It is clear that the rims are enriched in lead and silver, and that there is a general correlation between

the lead and silver contents. SEM-EDX analysis of many of the rims indicated them to consist of a Pb-Ag sulphide containing minor amounts of Zn and traces of Fe. The Zn and Fe may represent part of the underlying sphalerite particle. The mineralogical equivalent of the Pb-Ag sulphide is not known. Although the Pb-Ag sulphide appears single phase, significantly, Pb-Ag sulphides have not been reported in the mineralogical literature and the possibility exists that the rims may be an intimate mixture of PbS and Ag_2S.

Figure 18 indicates several medium to small iron-bearing sphalerite particles (medium grey) all of which are extensively rimmed by compact layers of Pb-Ag sulphide (white to light grey). Again, it must be emphasized that most of the sphalerite grains in this flotation concentrate are rimmed by this Ag-bearing sulphide phase.

5028 - FLOTATION CONCENTRATE FROM THE NEUTRAL LEACH RESIDUE IN THE CEZ STORAGE POND

X-ray powder diffraction analysis showed this concentrate to consist of major amounts of sphalerite and zinc ferrite.

Microscopic study (Figure 19) showed the concentrate to consist generally of fairly large sphalerite particles (light grey) in a fine matrix (medium grey) composed of major zinc ferrite and tiny sphalerite grains together with minor hematite and trace amounts of pyrite, quartz, chalcopyrite and silicates. A large silicate grain (5 x 20 μm, medium grey) is situated at the right-centre of the field shown in Figure 19. A porous hematite particle (light to medium grey, ∿15 μm) is found in the lower-left corner, and its texture suggests a roaster product, likely a calcined pyrite grain.

This concentrate assayed 0.25% Ag, and many silver-bearing grains were identified. In every instance, the silver seemed to be present as Ag_2S or $(Cu,Ag)_2S$ on the edges of sphalerite grains (especially the smaller particles) and as inclusions within larger sphalerite particles.

Figure 20a shows a larger sphalerite particle (light grey), the upper surface of which (porous, medium grey) is covered with Ag_2S containing a trace of copper. The relative concentration of silver along this face of the sphalerite grain is shown in Figure 20b.

Figure 21a is a smaller sphalerite grain (white) shown at high magnification. This particle contains a rim of $(Ag,Cu)_2S$ that is <1 μm thick and is clearly quite diffuse as evidenced by the AgL_α X-ray distribution map shown in Figure 21b. A high copper content is associated with the silver at the bottom-centre edge of the sphalerite grain. The complete encapsulation of the sphalerite coupled with the diffuse nature of the $(Ag,Cu)_2S$ layer supports the contention that the silver-bearing sulphide has been precipitated onto the surface of the sphalerite grain.

Figure 22a illustrates a large sphalerite grain (white or light grey) surrounded by a fine mixture of zinc ferrite and sphalerite (medium grey). In the centre of the sphalerite grain is a light grey mass about 10 μm in size which seems to consist of silver-bearing Cu_2S; associated with this Cu_2S mass is a hole (black) which is lined with copper-bearing Ag_2S. Figure 22b shows the relative distribution of silver in the sphalerite inclusion and Figure 22c indicates the corresponding relative copper concentration.

CONCLUSIONS

Two neutral leach residues and one high acid leach residue from zinc processing circuits were subjected to flotation to produce three silver concentrates. These six samples were examined mineralogically to determine their phase characteristics and to elucidate the mineral forms of silver.

The neutral leach residue from the CEZ storage pond consisted of zinc ferrite, sphalerite, quartz and hematite, often cemented together by an amorphous iron hydroxide possibly containing a Fe-Zn sulphate; no silver-bearing minerals were detected in this residue. The concentrate prepared from the pond residue consisted of major sphalerite and zinc ferrite together with minor amounts of hematite and traces of pyrite, quartz, chalcopyrite and silicates. This concentrate contained abundant silver as rims of Ag_2S or $(Cu,Ag)_2S$ on sphalerite; inclusions of these sulphides in the larger sphalerite grains were also seen.

The neutral leach residue from a pilot plant run consisted of fine-grained zinc ferrite, lead sulphate and sphalerite together with traces of hematite, magnetite and pyrite. Silver-bearing material was detected in this residue as an Ag_2S coating on one sphalerite grain. The flotation concentrate made from this residue consisted of sphalerite and zinc ferrite together with a trace of quartz. Many if not most of the sphalerite grains were rimmed by a continuous layer of Pb-Ag sulphide which may be a mixture of PbS and Ag_2S although the identity of this phase is not clear.

A high acid leach residue from Kidd Creek Mines was also examined and was found to consist of a jarosite-type compound, lead sulphate and sphalerite with minor amounts of hematite and zinc ferrite as well as traces of chalcopyrite, pyrite and gypsum. There is some evidence that the jarosite is silver-bearing, and silver was clearly evident in masses of sulphur-silica gel and as thin coatings on sphalerite. The silver was always closely associated with Se and was likely present as $Ag_2(S,Se)$. The concentrate prepared from the high acid leach residue consisted of a jarosite-type compound (likely Ag-bearing), sphalerite, elemental sulphur and possibly some lead sulphate together with minor to trace amounts of chalcopyrite, zinc

ferrite, quartz, cassiterite and barite. Silver was frequently detected, either as ill-defined masses of selenium-bearing silver sulphide closely associated with minor Si or as $Ag_2(S,Se)$ particles in elemental sulphur-jarosite clusters.

In this study, silver was generally present as the sulphide which was intimately associated with gel-like masses, sphalerite or other sulphides. Previous work suggests that silver is also contained in the jarosite phase seen in the high acid leach products. Chlorine was rarely detected and, on those occasions, it seemed to originate from glues, mounting media, etc., and not from silver chloride. The abundance of silver-rimmed sphalerite in some of the concentrates coupled with its comparative absence in the respective residues might indicate some mobility/concentration of silver during the actual flotation process.

ACKNOWLEDGEMENTS

The assistance of E.J. Murray and P. Carriere with the X-ray diffraction analyses is gratefully acknowledged.

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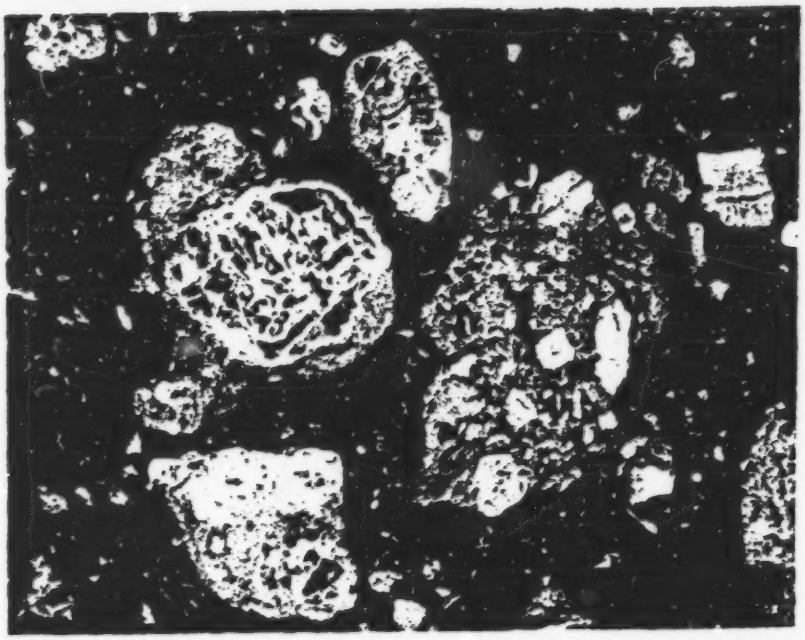


Fig. 1 - Backscattered electron micrograph of the neutral leach residue from the CEZ pond that illustrates the general aggregated morphology of the material.

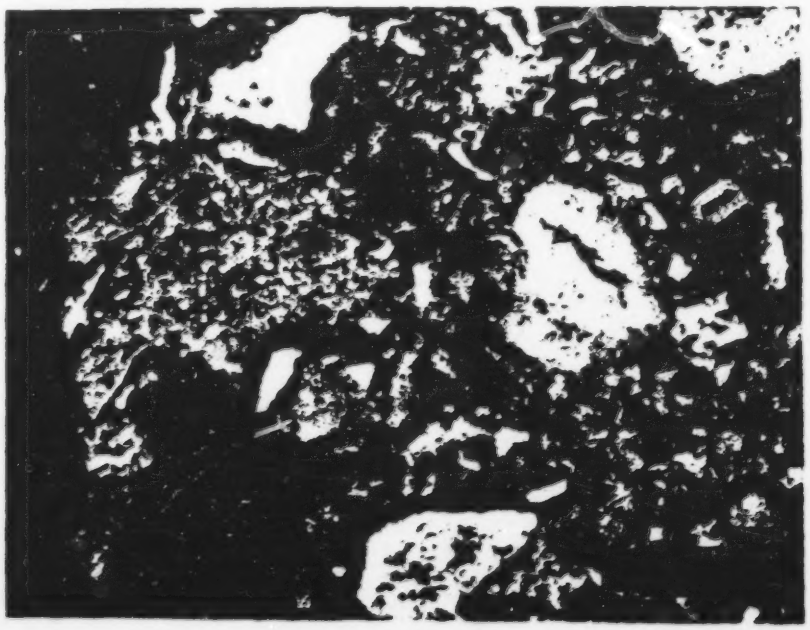


Fig. 2 - Secondary electron micrograph of one of the composite grains in the neutral leach residue from the CEZ pond.

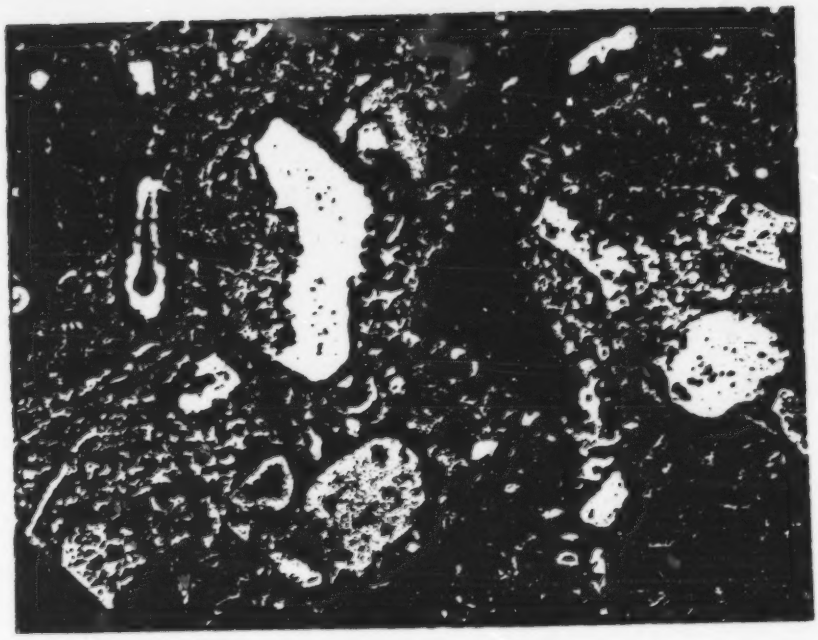


Fig. 3 - Backscattered electron micrograph of another composite grain in the neutral leach residue from the CEZ pond.

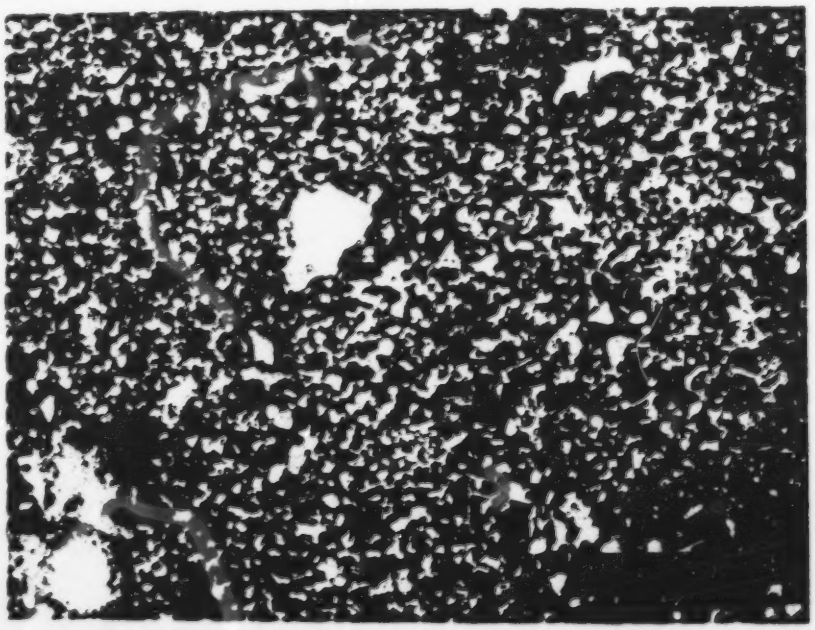


Fig. 4 - Backscattered electron micrograph giving a general view of the neutral leach residue from the Noranda pilot plant run.

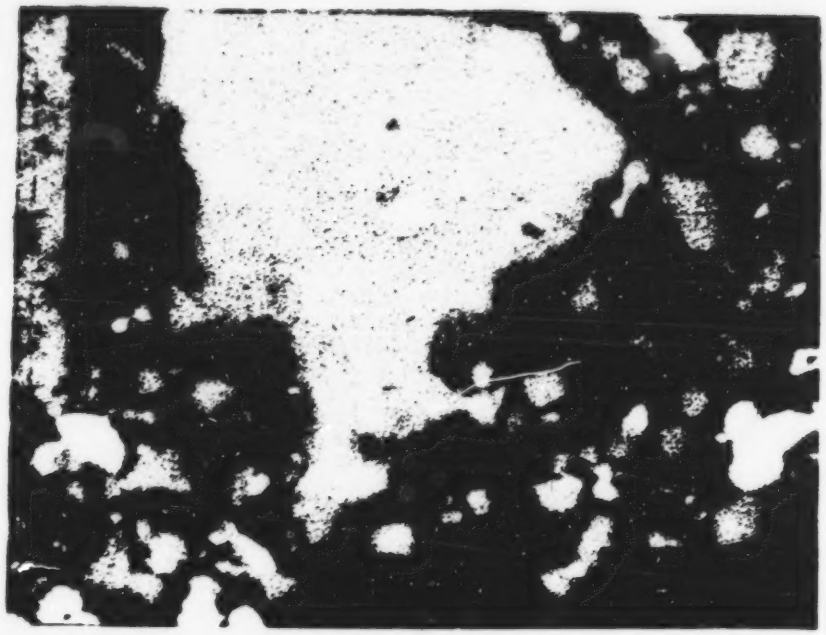


Fig. 5 - Backscattered electron micrograph of a large sphalerite particle in the pilot plant neutral leach residue that has a tiny zone of Ag_2S at the extreme lower tip.

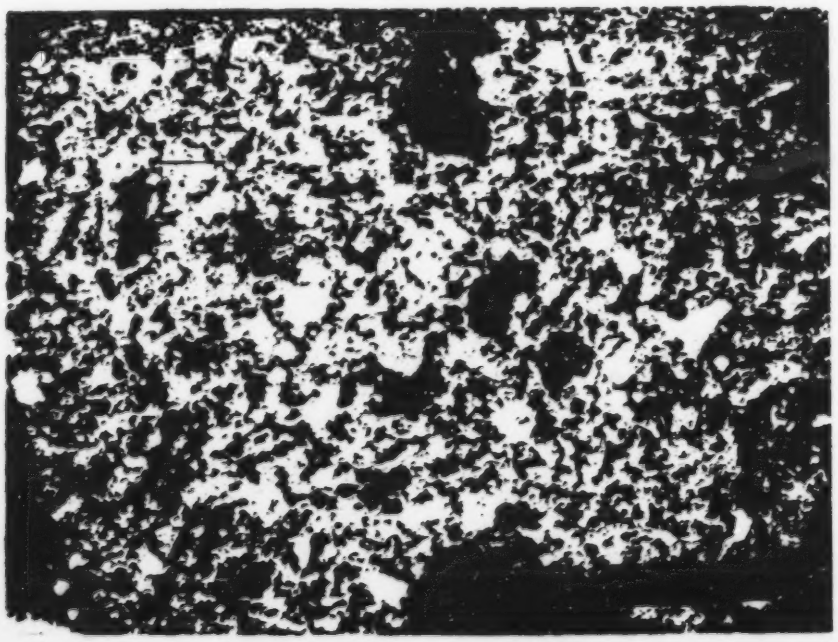


Fig. 6 - Backscattered electron micrograph of the high acid leach residue from Kidd Creek Mines that illustrates the general features of this material.

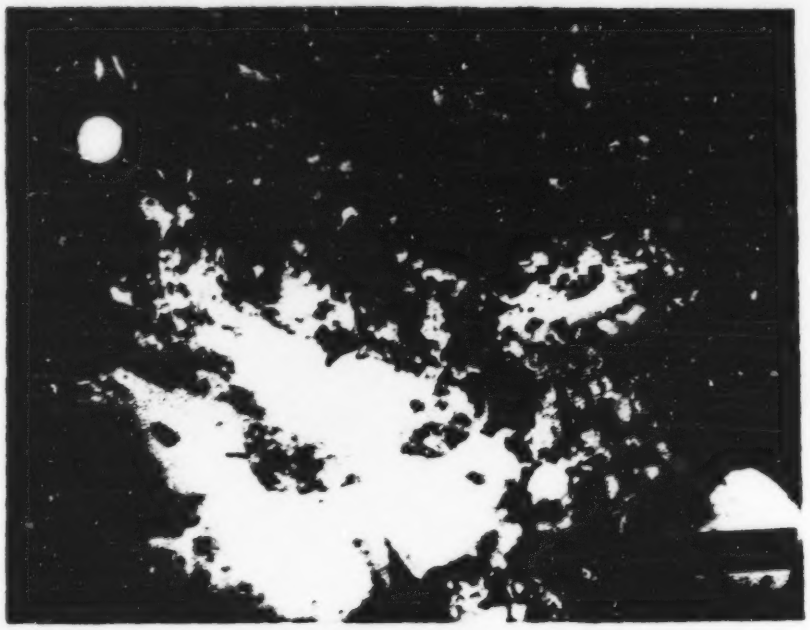


Fig. 7a - Secondary electron micrograph illustrating a Ag-bearing gel-like mass associated with a hole in the high acid leach residue from Kidd Creek Mines.

Fig. 7b - AgL_{α} X-ray map showing the relative concentration of silver in the gel-like mass of Fig. 7a.

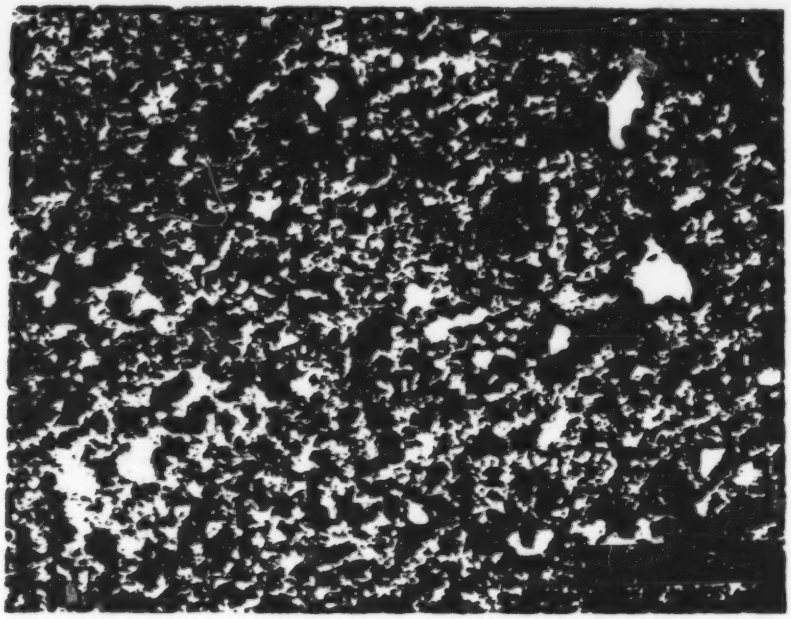


Fig. 8 - Backscattered electron micrograph showing the general characteristics of the flotation concentrate made from the high acid leach residue.

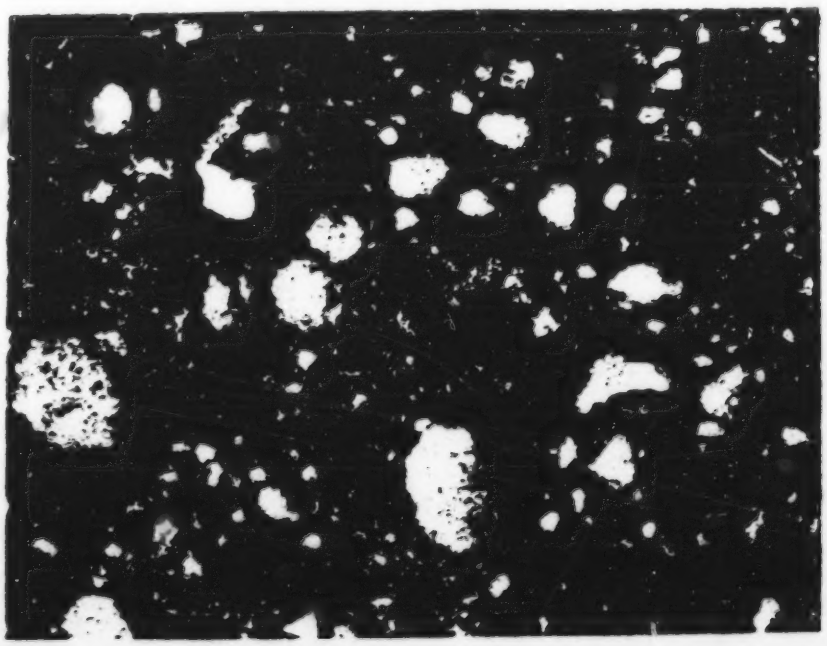


Fig. 9 - SEM micrograph of the flotation concentrate (in loose powder mount) made from the high acid leach residue, and showing abundant coarse grained sulphur clusters (light grey).

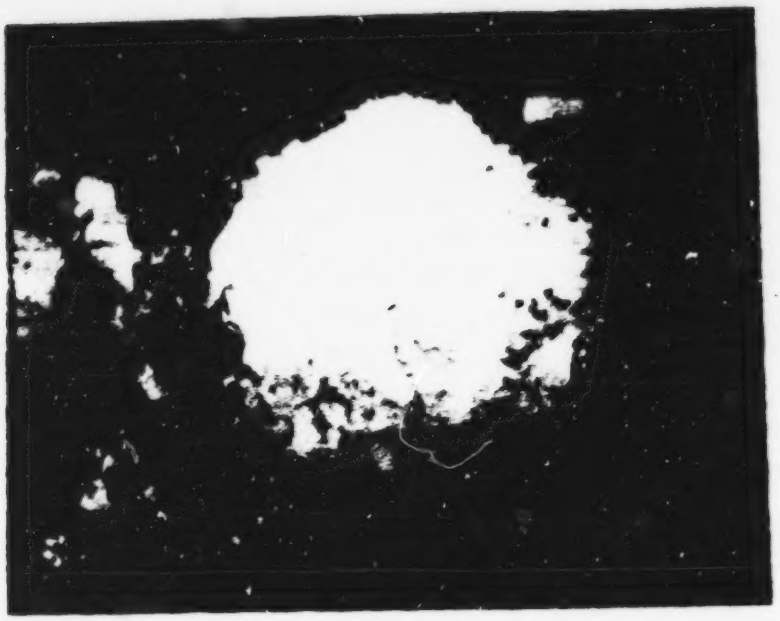


Fig. 10 - SEM micrograph of a sulphur cluster in the loose powder mount of the concentrate made from the high acid leach residue.

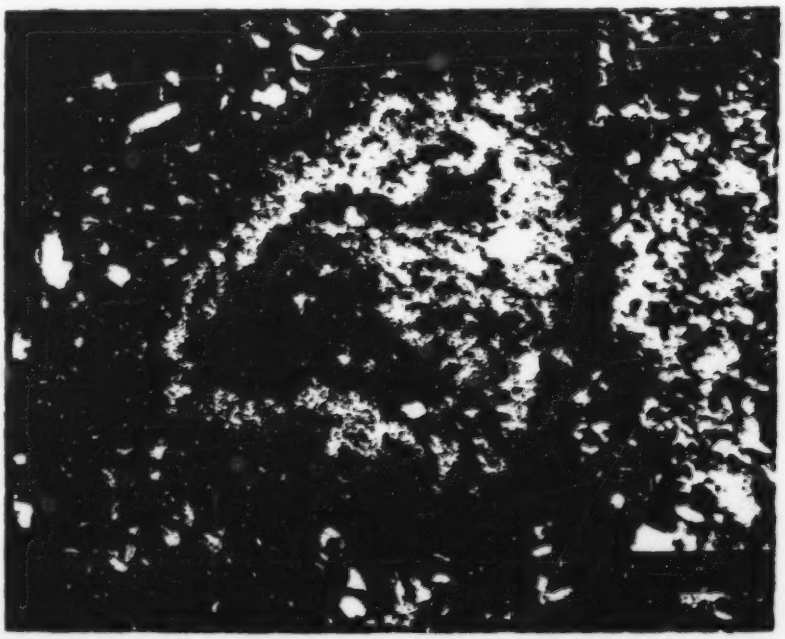


Fig. 11 - Backscattered electron micrograph of an ill-defined $Ag_2(S,Se)$ mass in the concentrate made from the high acid leach residue.

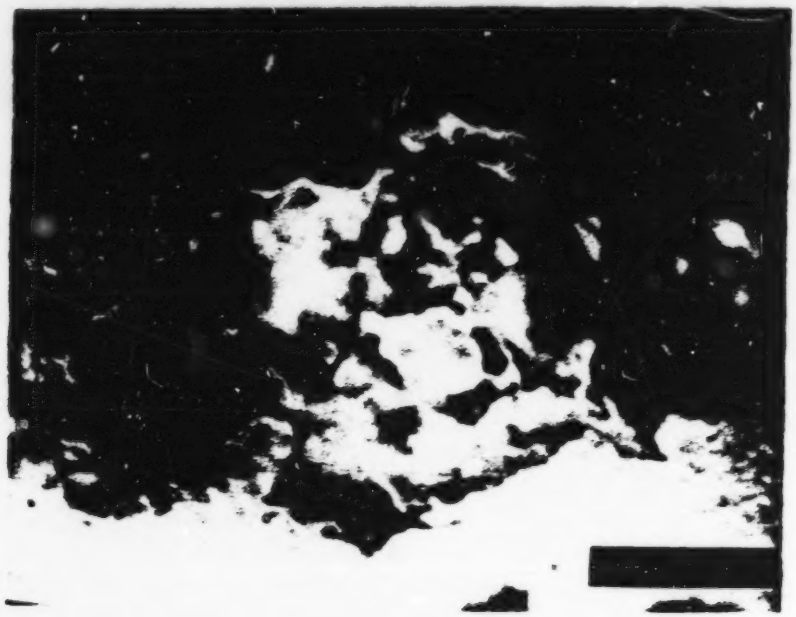


Fig. 13 - Secondary electron micrograph showing the detailed structure of a mass of $Ag_2(S,Se)$.

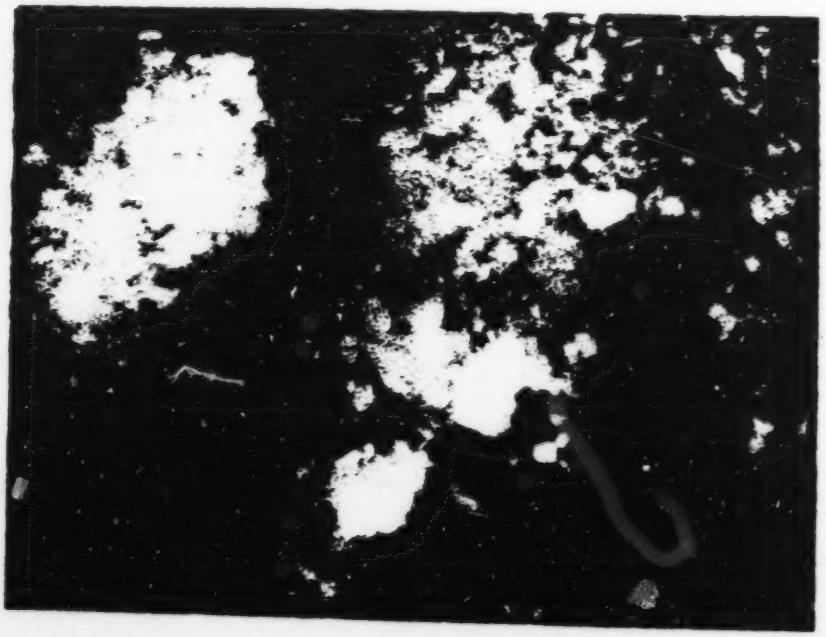


Fig. 14 - Backscattered electron micrograph of tiny $Ag_2(S,Se)$ particles (white) in a sulphur-jarosite cluster (grey). Loose powder mount.

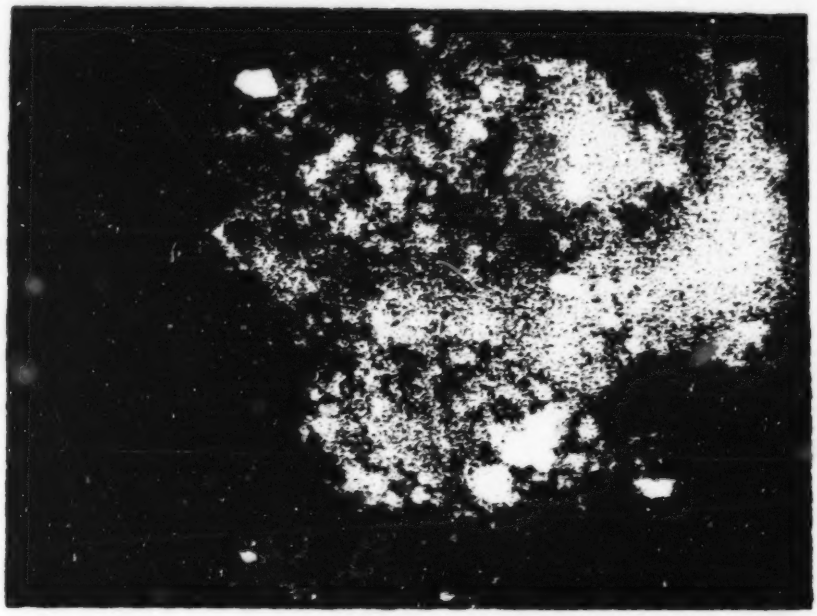


Fig. 15 - Backscattered electron micrograph of small $Ag_2(S,Se)$ grains (white) in large sulphur-jarosite clusters (grey). Loose powder mount.

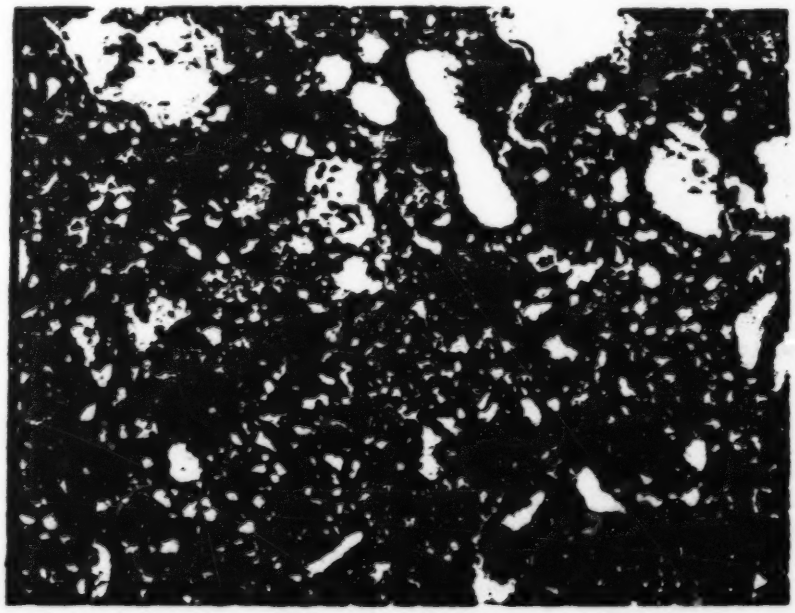


Fig. 16 - Backscattered electron micrograph showing a general view of the concentrate made from the pilot plant neutral leach residue.

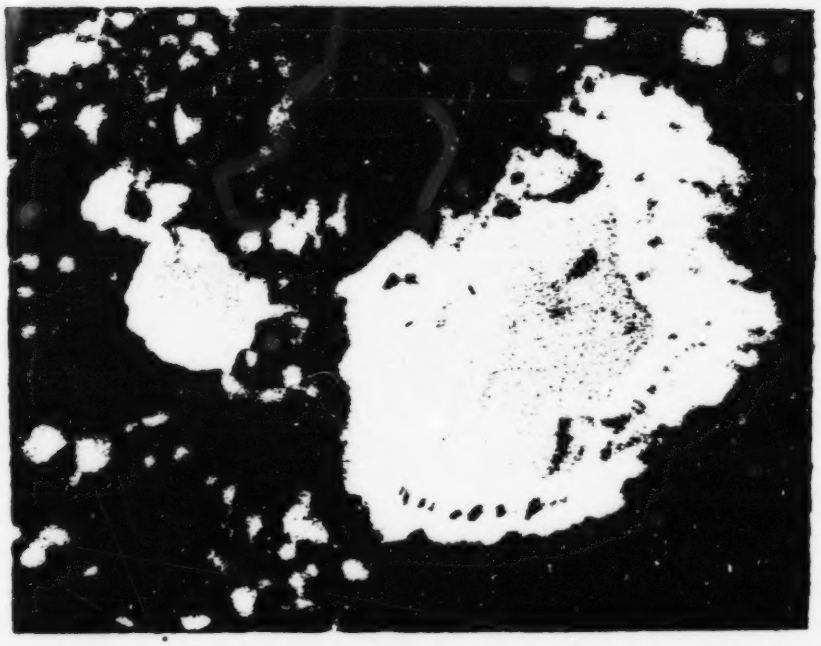


Fig. 17 - a) Backscattered electron micrograph illustrating sphalerite particles (medium grey) rimmed by Pb-Ag sulphide (white) in the concentrate made from the pilot plant neutral leach residue.

Fig. 17 - b) AgL_{α} X-ray map showing the relative distribution of silver in Fig. 17a.

Fig. 17 - c) PbL_{α} X-ray map showing the relative distribution of lead and its close association with silver in Fig. 17a.

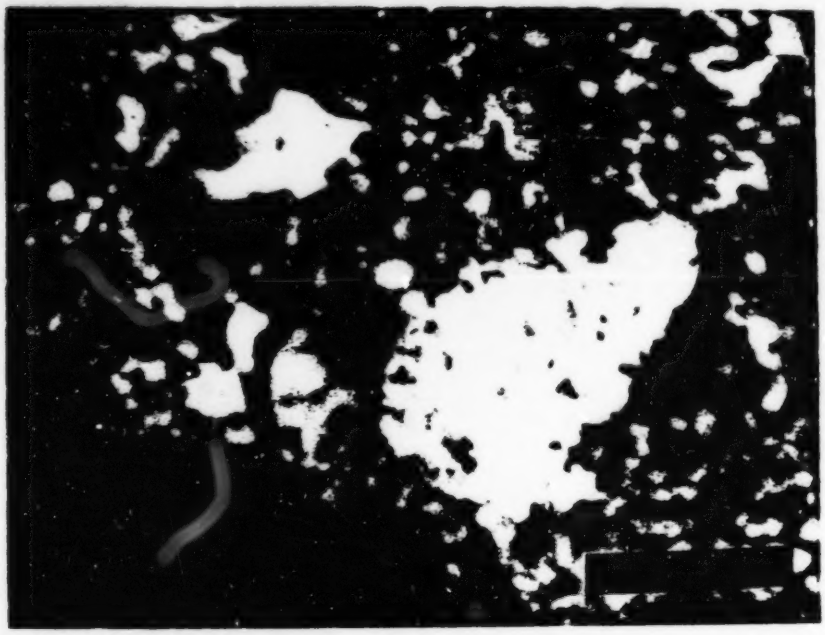


Fig. 18 - Backscattered electron micrograph of several smaller sphalerite grains (medium grey) all rimmed by Pb-Ag-sulphide in the concentrate made from the pilot plant neutral leach residue.

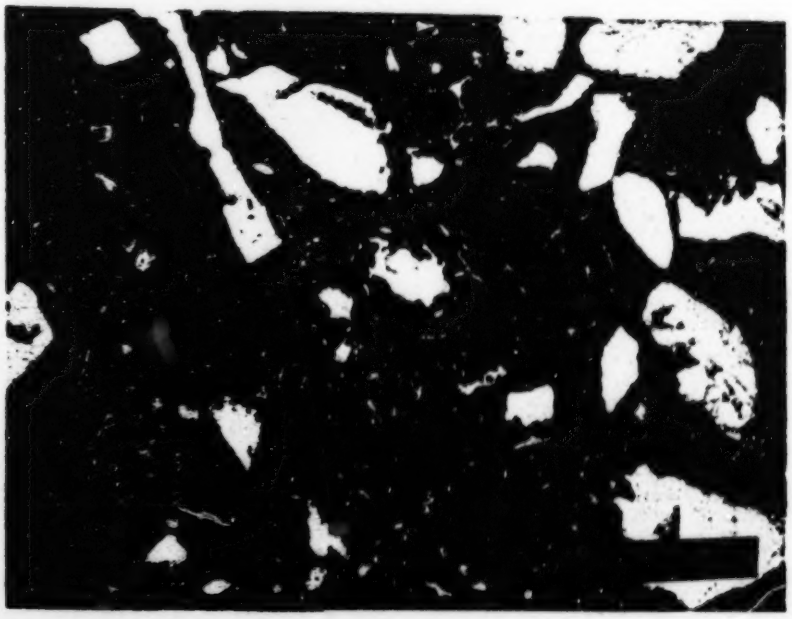
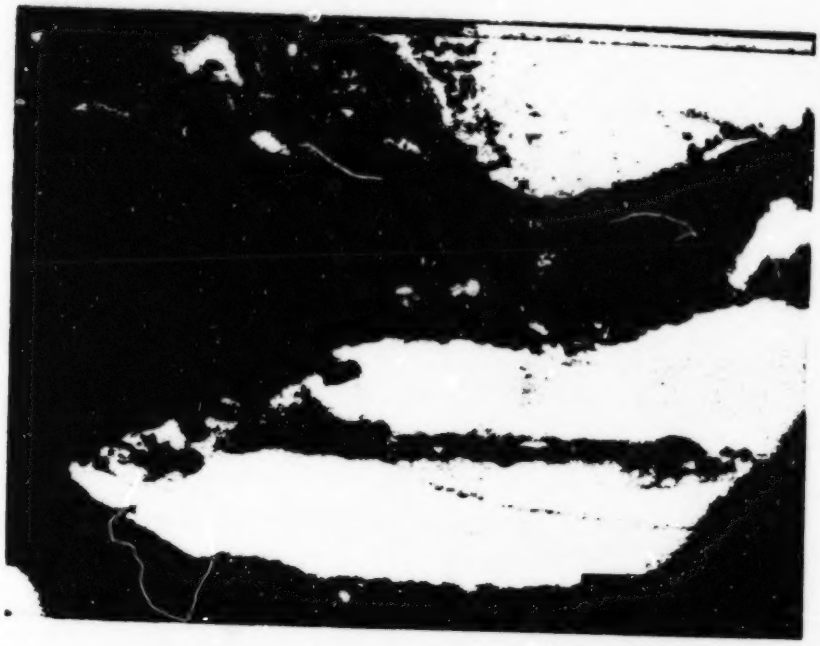


Fig. 19 - Backscattered electron micrograph showing a general view of the concentrate made from the neutral leach residue in the CEZ storage pond.



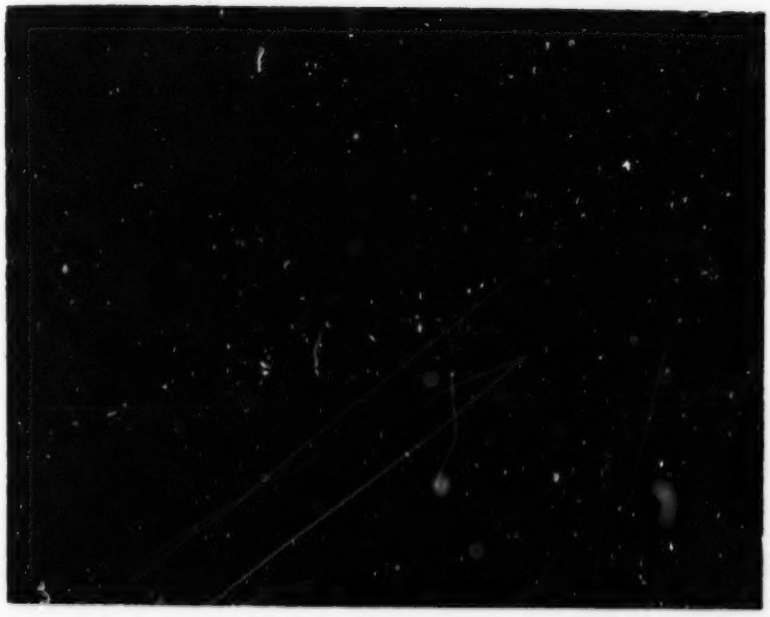
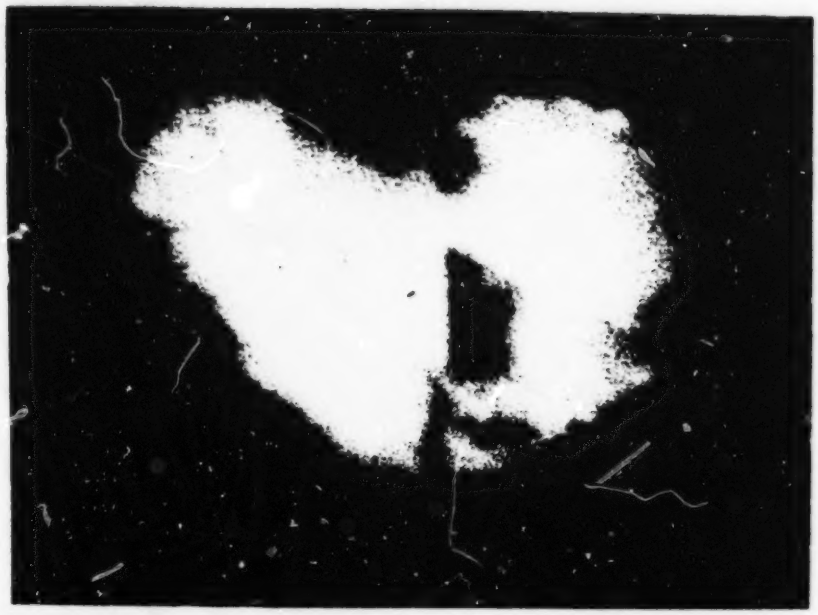


Fig. 20 - a) Backscattered electron micrograph of a sphalerite grain in the neutral leach residue from the CEZ pond. The upper surface is coated with Ag_2S (whiter).

b) AgL_α X-ray map showing the relative distribution of silver and its concentration at the top of the grain.



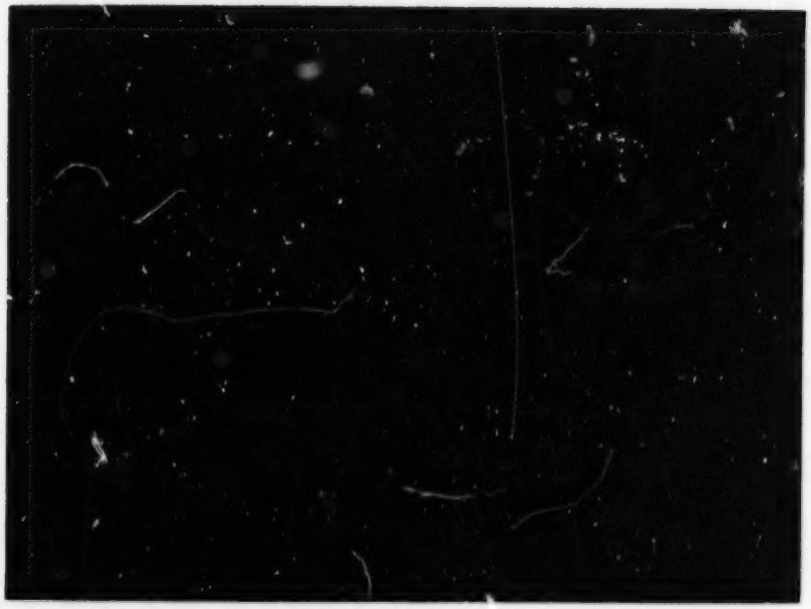


Fig. 21 - a) Backscattered electron micrograph showing a small sphalerite grain rimmed by $(Cu,Ag)_2S$ (light spots, porous) in the concentrate prepared from the neutral leach residue in the CEZ pond.

b) AgL_α X-ray map showing the diffuse distribution of silver about the sphalerite grain.

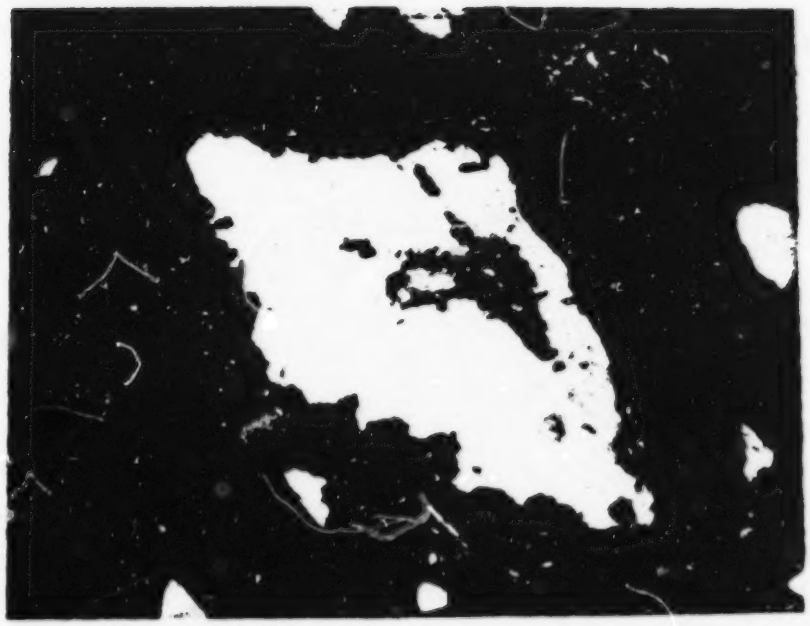


Fig. 22 - a) Backscattered electron micrograph of a large sphalerite grain (light grey) in the concentrate made from the neutral leach residue in the CEZ storage pond. In the centre of the grain is a composite inclusion of silver-bearing Cu_2S (medium grey) and copper-bearing Ag_2S.

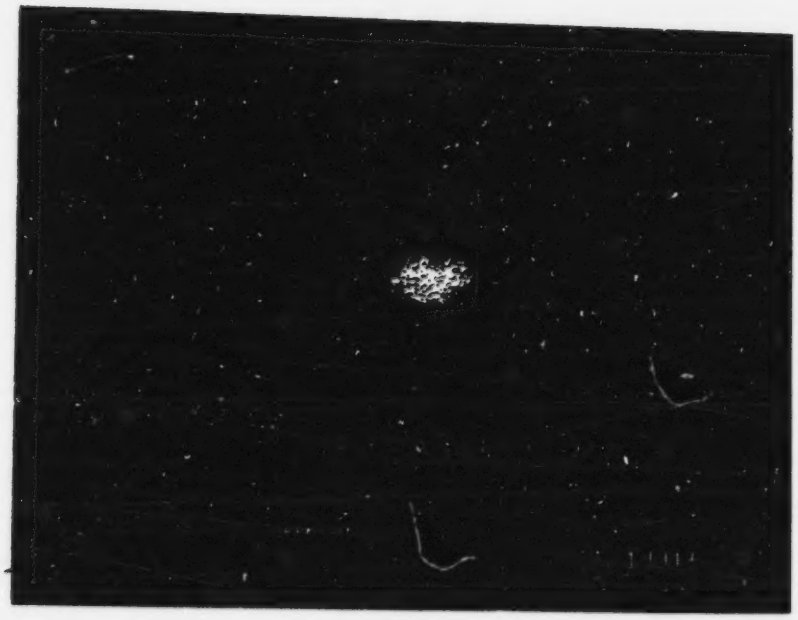


Fig. 22 - b) AgL_{α} X-ray distribution map showing the concentration of silver in the composite inclusion.

c) CuK_{α} X-ray map illustrating the concentration of copper in the composite inclusion.